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A STUDY TO ACHIEVE ENHANCED OIL DEGRADATION BASED ON COMPOSTING THE OIL WITH A BIOMASS PRODUCT

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A STUDY TO ACHIEVE ENHANCED OIL DEGRADATION BASED ON COMPOSTING THE OIL WITH A BIOMASS PRODUCT

FINAL REPORT

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EXECUTIVE SUMMARY

A preliminary study of degradation of oily sludges in closed reactors with leachate recycle was performed. Oily sludges from Husky Oil's conventional oil refinery at Prince George, B.C. and from the heavy oil refinery at Lloydminster, AB were used. Sludge was first treated with permanganate to oxidize complex aromatic molecules. The sludge was then absorbed into the peat product Oclansorb, mixed with bacterial culture and nutrients and allowed to degrade in reactor systems.

Microbial biomass rapidly increased in the reactors which generated a certain amount of heat. Degradation of oil in the sludge from conventional oil refining, as monitored by total oil recovery and gas chromatography, was observed mainly in the saturate fraction up to C35 size molecules. Sludge from heavy oil refining was degraded in the saturate fraction and also in the complex components of the oil which were not resolved by gas chromatography.

Heavy metals did not accumulate in the leachate implying that they were retained in the peat matrix. Polynuclear aromatic hydrocarbon compounds did not accumulate in the leachate waters implying that they were being degraded by microbial activity.

Permanganate did not oxidize the oil due to a low permanganate/carbon ratio and to the insolubility of permanganate in oil. However, apparent enhanced biodegradation of the complex components of the heavy oil sludge treated with 0.75 moles potassium permanganate/Kg sludge still implied the involvement of permanganate effects.

Although the results are preliminary, indications are that significant degradation rates were obtained in all cases. These will be verified in future studies. Preoxidation of oil before biodegradation still appears as an attractive aid for degradation of recalcitrant wastes. A search for a more effective oxidation system should be initiated to enhance degradation in the presence of Oclansorb.

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SOMMAIRE

Nous avons etudié la dégradation du pétrole dans les réacteurs fermés dans lesquels la filtration est recirculée. Nous avons utilisé les pétroles legers provenants de la raffinerie de Husky Oil de Prince George, B.C. and les pétroles lourds provenants de Lloydminster, AB. D'abord, les vases pétroleuses ont eté traitées avec du permanganate de potassium pour oxyder les molécules complexes aromatiques. Les vases ont eté absorbées avec le produit de la tourbe, Oclansorb. Puis on ajouté la culture bactérienne et du nitrogen et du phosphor. Ce mélange a eté mis dans les réacteurs pour que la degradation se procède.

Pendant six semaines les microbes s'augmentent dans les réacteurs et les réacteurs s'echauffent. La dégradation du pétrole leger fut obtenu en mesurant la quantite du pétrole recouverte. La chromatographie gaseuse a indiqué que les molécules jus qu'a C-35 de grandeur dans la fraction saturée du pétrole ont ete degradés. Quant au pétrole lourd, nous avons trouvé que la fraction saturée et aussi les composants complexes etaient tous les deux degradés.

Ni les métaux lourds ni les molécules aromatiques polynucleares hydrocarboniques s'accumulent dans la filtration.

Le pétrole n'a pas eté oxydé par le permanganate de potassium. Probablement c'est parce que le permanganate de potassium n'est pas dissolu dans le pétrole. Cepentdant, il semblit qu'il y avait plus de la biodegradation des composants complexs du pétrole en face de 0.75 moles permanganate de potassium/Kg pétrole. Cela indicat un effet du permanganate.

Les resultants sont préliminaires mais en tous cas un niveau éléve de la dégradation fut obtenu. Ces resultats seront verifiés en études futurs. Il se peut que d'oxyder le pétrole avant la degradation microbienne aidera la dégradation des molécules complexes. It faut chercher une méthode efficace pour oxyder le petrolee et accroître la dégradation de cétte pétrole avec Oclansorb.

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1.0 OBJECTIVE

To achieve enhanced oil degradation in a closed reactor vessel, based on composting the oil with a biomass product such as the heat-treated peat product, Oclansorb.

2.0 INTRODUCTION

Previous studies performed at NHRC have established that certain products of biomass origin (specifically a certain heat-treated peat moss product sold under the trade name Oclansorb) will stimulate oil degradation rates in lab scale experiments (1). Field test studies performed at a landfarm demonstrated increased oil degradation and increased oil degrading microbes in the presence of this product (2). In contrast, a commercial non-heat-treated peat supported less oil degradation and less microbial numbers in a field trial. Further field tests with Oclansorb in a reactor at Husky Oil's Prince George refinery demonstrated increased oil degrading microbes in the presence of this product, self heating and sustained operation at ambient temperatures below freezing (3).

An oil degradation system in a closed reactor was pinpointed as the next development stage in the hope that this would allow volatiles to be removed in a pretreatment prior to landfarming. Such a reactor might also allow pretreatment of recalcitrant heavy oils with oxidizing agents such as permanganate which has been postulated to promote hydrocarbon degradation (5). Success with such a system could lead to another field test specifically with heavy oil residues at the Lloydminster refinery and eventually be developed into a technology which could replace or be an adjunct to landfarming for disposal of such recalcitrant wastes.

3.0 METHODS

3.1 Materials

Oclansorb heat-treated peat was obtained from High Point Industries, Calgary, Alberta. Oily sludges were of two types. Tank bottoms from conventional oil refining were obtained from Husky Oil's Prince George refinery. Two samples of desalter sludge were obtained from Husky Oil's Lloydminster refinery. Carboys used to build the closed reactors were obtained from Fisher Scientific.

Three reactor vessels were constructed from 9 litre Nalgene carboys. A manifold was placed in each vessel for aeration of the mixture. Effluent gases from each vessel were scrubbed through a water trap

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located above each vessel to absorb water-soluble hydrocarbons (8). A second exit port at the back of each vessel allowed leachates to be removed from the bottom and recirculated through the top of the vessel. A schematic drawing of the reactors is shown in Figure 1. A picture of the reactors in operation is shown in Figure 2.

3.2 Sludge Pretreatment

Sludge samples from conventional oil refining were directly treated with solid potassium permanganate at various concentrations for 24 hours before assessment for changes to the sludge. After 24 hours, the samples were centrifuged to separate them into water and oil fractions. Each fraction was assessed by infrared spectroscopy and gel permeation chromatography for changes due to permanganate oxidation.

3.3 Reactor Loading and Mixing

After treatment with the appropriate concentration of permanganate, sludge samples (300 g) were added to 500 g Oclansorb and mixed until all the oil was absorbed into the peat. This mixture was then treated with nutrients and placed in the reactors. Air was bubbled through the reactors at a rate of 0.4 - 0.8 litres/min and the contents were mixed weekly. Samples were taken periodically for water, oil and microbial analysis.

The reactors were as follows. Reactor 1 contained tank bottoms sludge from Husky Oil's conventional Oil refinery at Prince George treated with 0.075 moles potassium permanganate/Kg sludge. Reactor 2 contained heavy oil desalter sludge #1 from Husky Oil's Lloydminster refinery treated with 0.075 moles potassium permanganate/Kg sludge. Reactor 3 contained heavy oil desalter sludge #2 from Husky Oil's Lloydminster refinery treated with 0.075 moles potassium permanganate/Kg sludge. A fourth modified reactor without an air stream manifold contained desalter sludge #2 treated with 0.75 moles potassium permanganate/Kg sludge to determine the effect of high permanganate concentrations on microbial growth.

3.4 Oil Analysis

3.3.1 Volatiles

Volatiles were trapped on glass columns (11.5 cm x 0.2 cm ID) containing carbotrap graphatized carbon black (20/40 mesh). Column traps were attached to the exhaust line at the water trap and

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gases allowed to flow through for 15 minutes. The column traps were then attached to a gas chromatography and thermally desorbed for 6 minutes at 310 degrees. The chromatograph was a Perkin Elmer Sigma 2000 equipped with an SPB-5 fused silica capillary column (30 m x 0.32 mm ID). The head pressure of the column was 75 kiloPascals and the splitter gas flow was 3 mL/min. The injector and detector temperature was 320 degrees. The instrument was programmed to run at 25 degrees for 7 minutes, 25 degrees to 40 degrees for 10 minutes, 40 degrees to 150 degrees for 3 minutes, 150 degrees to 300 degrees for 10 minutes and finally held at this final temperature for 5 minutes. Output of the data was on an HP3390A integrator with chart speed set at 0.4 cm/min.

3.3.2 Extracted Oil

Samples (50-100g) of Oclansorb/oil matrix were removed from the reactors for oil extraction and analysis. Oil extraction was performed by the technique of Dean and Stark (Appendix A) using hot dichloromethane. A portion (0.6 - 1.5 g) of the extracted oil was chromatographically fractionated on a column (1.5 X 50 cm) of activated alumina (chromatographic grade, 80 - 200 mesh). Elution was with successive washes of 100 mL heptane, 200 mL toluene, 100 mL 50% toluene/50% methanol and 300 mL trichloroethylene. The heptane and toluene cuts contained the saturate and naphthenic aromatic fractions respectively. These were rotovaporated to remove solvents and subjected to gas chromatography to obtain their characteristic fingerprints.

Gas chromatography was performed with a Perkin Elmer Sigma 2000 gas chromatograph equipped with an SPB-5 fused silica capillary column (30 m x 0.32 mm ID). The head pressure of the column was 75 kiloPascals and the splitter gas flow was 30 mL/min. The purge gas flow was 3 mL/min. The injector and detector temperature was 320 degrees. The instrument was programmed to run at 70 degrees for ten minutes, then increase the temperature by 10 degrees per minute up to 100 degrees, followed by a 3 degree per minute increase up to 300 degrees. The temperature was maintained at 300 degrees for 30 minutes. The output of the resulting data was on an HP3390A integrator with chart speed set at 0.4 cm/min. A one microlitre sample was use for injection.

Gel permeation chromatography (GPC) was performed on a Waters GPC system equipped with a refractive index detector and Waters 840 software. Ultrastyragel GPC columns with pore sizes of 10^4, 10^3, 500 and 500 Angstroms were used. The mobile phase was tetrahydrofuran flowing at 1.0 mL per min. The column temperature was 30 degrees and the detector temperature was 35 degrees.

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3.5 Water Analysis

Water analysis for the presence of polyaromatic hydrocarbons (PAH's) and specific elements was performed by Core Laboratories, Calgary, Alberta. PAH's were analysed by the EPA 625 method after extraction from the water with dichloromethane. Analysis was on an HP 5890 gas chromatograph and an HP 5970 mass spectrometer. Analysis of the elements in the water was performed after filtration with an Inductively Coupled Argon Plasma analyser (ICAP).

Alcohols in the water trap were analysed on an HP5890 gas chromatograph equipped with an SPB-5 fused silica column (30 m x 0.32 mm ID). The head pressure was 80 KPa and the splitter gas flow was 30 mL/min. The injector and detector temperature was 320 degrees. The instrument was programmed to run at 40 degrees, then increase the temperature from 40 degrees to 90 degrees at 15 degrees per minute, then hold at 90 degrees for three minutes. The output data was on an HP3393 integrator set at 1 cm per minute chart speed and attenuation at 2. A one microlitre sample was used for injection.

3.6 Microbial Analysis

Analyses of microbes in the reactors were performed by the most probable number technique. Replicate samples from each sampling time for each reactor were serially diluted from 10^{-1} to 10^{-12} in tubes of liquid culture medium and incubated for 14 days at ambient temperature. Turbid tubes indicating microbial growth were enumerated. These data were applied to standard probability tables published for this technique to estimate the number of bacteria per gram of compost material or per litre of leachate (4).

Minimal medium for enumeration of oil degrading organisms contained:

$K_2HPO_4.3H_2O$	13.1 g
$NaH_2PO_4.H_2O$	5.75 g
NH_4NO_3	2.0 g
$MgSO_4.7H_2O$	0.315 g
$CaCl_2.2H_2O$	0.0006 g
$FeSO_4.7H_20$	0.001 g
Distilled water	1 L

Final pH = 6.8

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Complex medium used to test for growth of total bacteria contained:

Peptone	0.4 g
Yeast extract	0.4 g
Glucose	0.96 g
$MnSO_4$	0.5 g
Distilled water	1 L

These media were dispensed 4.5 mL per tube. After the tubes were inoculated, 50 microlitres of Amauligak crude oil were added to each tube of minimal medium. Organisms which grew on and degraded the oil turned the tubes turbid and dispersed the oil.

4.0 RESULTS

4.1 Sludge Pretreatment

Initially, sludge from the Prince George refinery was treated with 0, 0.00075, 0.075 and 0.75 moles potassium permanganate/Kg sludge by mixing this chemical directly with the oil in a blender and allowing the mixture to react for 24 hours. The treated oil was then centrifuged at 30,000 X G for 1 hour and the water removed and analysed for permanganate by UV absorption at 525 nm. From these studies 0.75 moles permanganate left high residual chemical after reaction and it was feared that this would be detrimental to bacterial growth. Therefore the next highest concentration of permanganate (0.075 moles/Kg sludge) was used to treat the oil for further study. Even at this concentration trace amounts of permanganate could still be deleted in the water fraction after 24 hours.

Centrifugation fractionated the oil into a light oil condensate, waxy, waxy plus solids and water fractions (Figure 3). The waxy layer appeared to increase with increasing permanganate treatment. However, infrared spectra and analysis by GPC failed to show any significant changes in the oil with increasing permanganate treatment (Figures 4 and 5). In particular, no evidence of partial oil oxidation was observed by IR Analysis.

Changes were observed in the water fraction of the oil after permanganate treatment. A peak located at 250 nm of the UV spectrum decreased on treatment with increasing permanganate (Figure 6). This peak is characteristic of aromatic ring structures somewhat similar to naphthalene which reacted in the same manner on treatment with permanganate (Figure 7). Infrared analysis of the extract of the water

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fraction showed minor changes with treatment (Figure 8). A peak at 1100 cm^{-1} had less intensity after treatment.

4.2 Reactor Temperature

The temperature in reactor 1 rapidly increased and stabilized at 4° - 5° above ambient. The temperature in reactors 2 and 3 increased more slowly and stabilized at 2° - 3° above ambient (Figure 9).

4.3 pH Changes

The initial pH of the water in the reactors was buffered at pH 6.8. Addition to peat decreased the pH to close to 5.0. Over time this again increased to 6.0 - 6.2.

4.4 Water Analysis

4.4.1 Reactor 1 (Prince George Sludge)

The leachate waters from the Prince George sludge in reactor 1 contained bi and tricyclic hydrocarbons at the 5 microgram per liter level at week 4 (Table 1). Levels were at 140 - 210 microgram per litre by week six but were reduced to the 5 microgram level by 10 weeks.

The water trap on the effluent gas line contained minor amounts of chrysene and triphenylene only and no alcohols were present.

At six weeks levels of heavy metals of cadmium, chromium, lead, nickel, vanadium and zinc were low and were no higher than those in the other reactors sampled at this time. Calcium, magnesium, manganese, phosphorus, potassium and sodium levels were lower than in the other reactors (Table 2) suggesting more biological activity in this reactor had sequestered them as nutrients.

4.4.2 Reactor 2 (Lloydminster sludge #1)

The leachate water from the Reactor 2 containing desalter bottoms #1 from Lloydminster showed a general increase in PAH's in the six week sampling compared to two weeks. Only naphthalene showed a decrease over this time period (Table 3).

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The water in the effluent gas trap contained trace amounts of chrysene/triphenylene. No alcohols were found in the trap.

Heavy metals cadmium, chromium, lead, nickel, vanadium and zinc did not show significant changes in their level over the period of the study (Table 4). There was an increase in levels of calcium, magnesium, phosphorus, potassium and sodium over the period of the study.

4.4.3 Reactor 3 (Lloydminster sludge #2)

The leachate water from Reactor #3 containing desalter sludge #2 from Lloydminster contained the two aromatic compounds naphthalene and methylnaphthalene (Table 5). No higher ring number compounds were quantitatively identified.

The water trap from the effluent gas line contained no PAH compounds or alcohols.

Metals in the leachate did not show significant changes in cadmium, chromium, lead, nickel, vanadium or zinc (Table 6). Magnesium, manganese, calcium, sodium , potassium and phosphorous all decreased at the end of six weeks compared to two weeks.

4.5 Oil Recovery

4.5.1 Volatiles

The volatile gases escaping from each reactor varied over time. Oil in reactor 1 showed a steady change in the composition of the volatiles until at 5 weeks, most of the volatiles had been stripped (Figure 10). The volatiles from the heavy oil desalter samples in reactors 2 and 3 contained less light ends than the Prince George samples. However, these volatiles were readily stripped over a period of five weeks.

4.5.2 Extracted Oil

Oil was extracted from reactor samples in two ways. First, Dean and Stark extraction was performed as samples were collected. The amount of oil recovered from the reactor samples was highly variable. In some cases the percent oil actually increased rather than decreased. Cases of oil increase correlated with the personnel performing the extraction suggesting operator error for these data (Table 7A, B and C). The second set of assays performed on stored samples collected from each reactor at the

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beginning and end of the study showed 34%, 55% and 38% oil loss at six weeks in reactors 1,2 and 3 respectively. Disregarding the suspect results and including the data from the second extraction set implied a steady oil decrease in all reactors over the experimental period (Figure 11).

4.5.3 GC Profiles of the Recovered Oils

4.5.3.1 Reactor 1 (Prince George sludge)

A comparison of the oil fingerprints over the study period showed a progressive loss in all components of the oil (Figure 12). Most striking was oil loss in the region of C-20 - C-35. As the oil was degraded high molecular weight waxes (C-36 - C-42) became more prominent and contributed to a large amount of the chromatogram. For example, at week 1 the major component eluted at 63.54 minutes corresponding to C-31 alkane. At 6 weeks the major component eluted at 89.53 minutes corresponding to C-38 alkane (Figure 12).

The presence of high molecular weight relatively insoluble waxes in this sludge impeded accurate fractionation into saturate and aromatic fractions as these waxes were not leached from the alumina chromatography column in a consistent manner and contaminated the aromatic fractions.Consequently, gas chromatograms of these fractions were not prepared.

4.5.3.2 Reactor 2 (Desalter sludge #1)

GC patterns of the total oil recovered from the reactor showed that the bulk of the material is not resolvable by gas chromatography (Figure 13). However, over the period of the study resolvable components were lost from the chromatograms. Gas chromatography of the saturate fraction of the oil showed decreased intensity of the peaks at six weeks but complete absence of peaks indicating total degradation of components was not observed (Figure 14).

With the naphthene aromatic oil fraction, peaks disappeared and others appeared over the seven week period especially at 54.5, 58, and 70 minutes of the chromatogram (Figure 15).

4.5.3.3 Reactor 3 (Desalter sludge #2)

Gas chromatography of the total oil recovered revealed that peaks appeared and then disappeared over the time period (Figure 16). The saturate fraction of the oil showed a gradual decrease in peak

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intensities overall (Figure 17). The naphthene aromatic fraction also showed a general decrease in intensity but specific peaks were lost at 68 and 72.5 minutes of the chromatogram (Figure 18).

4.5.3.4 0.75 moles/Kg Potassium Permanganate-Treated Desalter Sludge

The GC pattern of desalter sludge treated with 0.75 moles/Kg potassium permanganate indicated degradation by decreased intensities of peaks at 60 - 79 minutes of the chromatogram over a six week period (Figure 19). Loss of total oil from the reactor over this period was 46% by the second extraction method. The recovered oil was not fractionated into saturate and naphthene aromatic cuts.

4.6 Microbial Analyses

Microbial growth in all reactors rapidly increased over time and reached a plateau. Oil degrading bacteria also increased with time and dominated the population (Figure 20). At four weeks the number of oil degrading and total bacteria in all reactors decreased. This decrease correlated with a bloom of protozoans. The number of bacteria reached the same level in all vessels. There were more bacteria associated with the solid matrix of Oclansorb and oil than free in the aqueous environment (Figure 20). There were few microbes in the water traps, but up to 10^7 organisms per mL were present in the condensate in lines leading to the traps. The high permanganate concentration used to treat the desalter sludge #2 in the fourth modified reactor did not have a detrimental effect on microbial growth. Microbial numbers in this reactor were as high as in the other three reactors.

5.0 DISCUSSION

5.1 Sludge Pretreatment

Indications of the beneficial effects of pretreating hydrocarbons prior to microbial degradation come from work performed at the Institute of Gas Technology in Chicago. Srivastava and coworkers reported a decrease in polyaromatic hydrocarbon concentration after permanganate treatment. This was due to chemical oxidation of the molecules. It was suggested that pretreating polyaromatic hydrocarbons with oxidizing agents would probably enhance biodegradation by causing a break up of larger molecules to reduce their size making them more available to degrading microorganisms (5). The present study indicated that permanganate oxidized the aromatic ring of naphthalene and by extension other complex ring structures in the oil samples used. The effects of permanganate on other oil components are unknown. Treatment with oxidizing agents may have positive effects by partially oxidizing PAH's to allow attack by organisms in subsequent treatment.

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Oxidation of aromatic rings in the water fraction of the Prince George sludge after permanganate treatment indicates that the treatment at lease works on PAH's and is concentration dependent. However, IR analysis failed to show changes in the oil fraction after treatment although there was excess permanganate left in the oil. Calculations revealed that the amount of permanganate used would react with 1/1000 - 1/100 carbon atoms assuming no reaction with contaminating substances. This is too low to be measured by IR analysis. Excess permanganate left in the oil after 24 hours indicates that the reaction may also be too slow to effectively oxidize the oil. Oxidation of naphthalene in water occurred in minutes while naphthalene solubilized in hexane showed no changes in its UV spectrum on treatment with permanganate (Appendix D). This implies that water-soluble organics will be attacked preferentially. Since permanganate is not soluble in organic solvents, and by extension in oil, the concentration used in this study would have affected a very small fraction of the total oil reflecting the low solubility of oil in aqueous environments.

The fate of the excess permanganate still present in the oil when it is added to the Oclansorb is unknown. It may have reacted with the Oclansorb immediately or may have been absorbed and released slowly to affect the PAH's as they solubilized. This should be investigated further as it has implications for future treatments with other oxidizing agents as well.

The observation of an increased waxy layer in the oil from both refineries after permanganate treatment may be due to partially oxidized hydrocarbons which are no longer soluble in the oil or to oxidation of emulsifiers which kept the waxy materials solubilized. It is generally believed that oil oxidation produces more complex tarry products and oxidation of preexisting oil is believed to have produced the tar sands (6,7). This is difficult to quantify and was not confirmed by changes in molecular size of the whole oil on GPC analysis. However, this was the only consistent observable change in both heavy oil sludge and conventional oil sludge after permanganate treatment. It appears that this permanganate treatment is not harsh enough and a better method of oxidizing the oil is required.

In future, an oxidizing system which is effective in an oleophilic environment or some means of treating the oil without deleterious affects on the degrading microbes should be sought.

5.2 Reactor Temperature

The temperature in all the reactors increased above ambient. This implied self heating of the reactor vessels due to microbial activity. Temperatures may have been higher than recorded but air passing through the units contributed to cooling. Operating temperatures in the reactors containing sludge

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from heavy oil refining did not reach that of the conventional sludge. This should not be due to reduced microbial activity in these reactors as the microbial numbers had increased to similar levels in all reactors. Possibly heat produced by microbial metabolism was used to help oxidize the complex molecules. A more reliable index of the heat evolved might be obtained by calorimetry and could be related back to the amount of carbon and, by extension, the oil which has been utilized.

One criticism of degradation in a reactor is that the heat generated will select for a thermophilic population which may have limited substrate and species range (8). In the present study the air fed into the system prevented the temperature from reaching the thermophilic range. With the present system, self-heating could allow it to operate longer than usual in a field application. A reactor located at the Prince George refinery was active and maintained its temperature above freezing against an ambient of minus 5 degrees centigrade for several weeks (3). This is an exploitable advantage as it could allow reactors to operate in the field for many months without applying additional head at colder temperatures. Future studies will have to address cooling due to air entry and control of the reactor temperature.

5.3 pH Changes

Oclansorb, being a peat derivative, is an acidic material and thus conferred an acidic environment to the reactors. Microbial activity and the buffer used in the system helped raise the pH to 6.0 - 6.2. This is still an acidic environment. Conventional wisdom states that optimum oil degradation takes place at pH 7.0 (10, 11). Nonetheless, high oil degrading microbial numbers and oil degradation was observed at this pH. There are indications that some oil components including PAH's may be more easily degraded at acidic pH (12). Previous studies showed that Oclansorb initially lowered the pH of the medium but the pH eventually increased to pH 6.5-6.8 (1,2). In those studies, the amount of Oclansorb used was less than in the present study. Acidic materials released from the peat may have been consumed as the pH returned to normal or the reactor may have been buffered by production of more basic microbial products. In this study, with the relatively large amount of peat used, a longer time will be required to raise the pH. However, oil degradation at acidic pH is of interest and future studies should investigate the effect of pH on oil degradation in the presence of Oclansorb.

5.4 Water Analyses

The water traps contained very little material. Only traps 1 and 2 contained minor amounts of the four ring compounds chrysene and triphenylene. Alcohols were not present in any of the reactors. Lighter PAH's like naphthalene and phenanthrene are not likely to be trapped due their volatility. Dibble

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reported soluble hydrocarbons were condensed in the water trap but did not identify them (8). The lines leading to the traps were contaminated with a population of oil degraders which may also have degraded these compounds as they passed through on the way to the trap. Water traps appear unnecessary and should be replaced with samplers to identify the specific hydrocarbons volatized from the reactors.

The water in the leachate from the reactors contained more material than the traps although the overall concentrations of PAH's were low. Quantification of this material is difficult due to volume changes over the course of the study. Concentrations of PAH's are generally in the order of tens to hundreds of milligrams per kilogram of oily sludge while solubilities are in the order of 0.004 to 30 mg/L of water (12, 13). PAH's are not known to be readily degraded in soil (12, 13, 14) and should accumulate. These levels are much greater than those found in the reactors in the present study indicating degradation in the reactors. While reactor 3 lost PAH's between week 2 and week 6, those in reactor 2 appeared to increase. Variability may be due to changes in PAH degrading populations within the reactors. The leachate in reactor 1 contained abnormally high concentrations of PAH's at week 6. This result may be erroneous as sampling a few weeks later did not show these high levels. Conversely, they may have been consumed by the second sampling time.

Elemental analysis showed a decrease in free metals in solution over the time period and may reflect their incorporation into microbial biomass. Analysis of the oil processed at the Lloydminster refinery established levels of nickel and vanadium at 60 and 230 mg/L while chromium was at 0.26 mg/L (15). Since the levels of these heavy metals in the reactor leachates were many times less, they are probably retained by the Oclansorb when the oil is degraded. The manganese used to treat the oil should result in 347 mg/L in the reactor. The amount found in the leachate was one hundred fold less indicating manganese retention by the Oclansorb also or formation of manganese species which are insoluble in the leachate.

5.5 Oil Recovery and Analysis

5.5.1 Volatiles

Loss of volatiles from the reactors over a five week period could be due to air stripping or microbial activity or to a combination of both. Air stripping could be controlled by condensing the exhaust and recycling organics to the reactor or by appropriate scrubbers. It could also be reduced by controlling the amount of air throughput. Increased air flow may be one way to rapidly strip volatiles from the sludge before degradation in the reactor. Quantification of the volatiles might allow a computation of

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the amount of material lost due to volatility. This should be addressed in future studies through use of traps and assays for specific volatile compounds.

5.5.2 Extracted Oil

Problems were encountered in obtaining accurate, reliable and quantifiable oil from the reactors. Variability in sampling does occur (9,12) but the Oclansorb and sludge were initially homogenized to minimize this problem. Refluxing times during the Dean Stark extraction procedure are very important especially where the sludge contains a lot of waxy material which is not readily extracted. Inadequate and variable timing of extraction contributed to some of the anomalies encountered where the amount of recovered oil increased then decreased and then increased over the course of the study. A repeat extraction of samples from the start and the end of the study by method 2 established 38% - 55% degradation occurred over the six weeks of the study. It must be stressed that these results indicate a trend and we do not possess enough information to statistically test the validity or variability of the data. External to this contract, the reactors will be sampled once more and careful analysis performed to verify these results. Future studies should address sampling variability and oil dispersion in the reactors. Standardized protocols for the oil extraction incorporating internal standards should be devised and followed.

In spite of the discrepancy, oil loss was also evident in the chromatograms over the study period. The removal of the low molecular weight alkanes from the sludge in reactor 1 correlated with degradation, total oil loss and heat generation. Similar patterns of oil loss and heating effects were obtained with the field scale reactor at the Prince George refinery.

The heavy oil sludges used in reactors 2, 3 and 4 all showed loss of a hump at 60 - 79 minutes of the chromatogram of the total oil corresponding to complex molecules probably containing ring structures. Loss of this hump was most striking in the presence of 0.75 moles potassium permanganate/Kg oil treatment where it appears to be degraded in preference to the lighter materials. Interestingly, the loss of this hump occurs gradually with time and not instantaneously. This implies that the permanganate or some other manganese species, and the microbes may be playing a part in the oxidation of these materials. Excess permanganate which did not initially react with the oil may be bound by the Oclansorb and released slowly to perform its oxidative function or microbes may be performing some complex mechanisms involving manganese.

This study did not contain controls for permanganate-free degradation. A reactor at the Prince George refinery obtained 1% - 20% degradation in 6 - 8 weeks in the absence of permanganate (3). However,

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results from the two studies are not directly comparable due to temperature and aeration rate differences. Appropriate controls must be included in future trials.

5.6 Microbial Analysis

Total oil degraders and total microbial numbers rapidly increased in all the reactors. While this is encouraging the rapidity of the increase was unexpected. All reactors were seeded with a microbial culture culled from the landfarm at the Prince George refinery. This culture is thus adapted to degrading lighter oil. The rapid initial microbial growth is probably based on degradation of the lighter ends of all the oils used in this study.

The microbial numbers remained relatively constant throughout the course of the study except for a decrease in numbers at four weeks. This decrease correlated with a bloom of protozoa which may be feeding on the bacterial culture. A check of the sludge samples indicated that these were the source of the protozoa at least in the cases of the samples from Lloydminster. Many species of protozoa graze on microbial blooms and the level of grazing may reflect the pH and nutritional conditions of the system (16). A reactor system subject to grazing may result in greatly reduced microbial numbers and thus reduced degradation efficiency. Onset of protozoan blooms and indices of their overall effect should be monitored. Relative constancy of microbial numbers in the reactors during the study implies that a varied microbial population was developed capable of using the molecules present in the heavy oil sludges as well as aliphatics and high molecular weight waxes present in the sludge from conventional oil refining at Prince George.

Few fungi were observed in the MPN tubes used to enumerate the bacteria in the reactors. In spite of recent reports implicating fungi in oil degradation, it appears that the majority of degraders in this study were bacteria. However the involvement of fungi cannot be ruled out entirely since some fungi have pleomorphic forms which could resemble bacteria and yeasts and need to be identified microscopically. Additionally, the media used for microbial enumeration would have discouraged fungal growth.

More microorganisms were associated with the matrix of oil and Oclansorb rather than being planktonic in the aqueous environment. This confirms previous observations obtained with the reactor at the Prince George refinery. Since the energy source is oil absorbed into the peat it is logical that the oil degraders should be associated with it.

This study did not specifically enumerate organisms capable of growing on PAH's. Concerns about landfarming partially centre on accumulation of these compounds since they are supposedly not readily

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degraded but instead accumulate in the soil and are leached to the groundwater (12,13,14). Since high levels of PAH's did not accumulate in the leachate from the reactors, the microbial culture which developed must have been capable of degrading them. Future studies should enumerate the organisms able to attack these species.

It was originally believed that high concentrations of permanganate would be too toxic for the microorganisms and the studies were therefore performed at 0.075 moles permanganate/Kg sludge. However, the organisms thrived and degraded oil in the reactor containing 0.75 moles permanganate/Kg sludge. The Oclansorb may have protected the organisms from the toxic effects of the high concentrations of this compound. In high concentrations of permanganate significant degradation was evident through changes in peaks at 60 -79 minutes of the chromatogram where more complex molecules are eluted. Future studies should be higher concentrations of permanganate and harshen treatment conditions.

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6.0 CONCLUSIONS

1. High numbers of oil degrading bacteria were established in lab reactors containing oily sludges from conventional and heavy oil refining pretreated with potassium permanganate at 0.075 moles and 0.75 moles/Kg sludge.

2. A high concentration of potassium permanganate (0.75 moles/Kg) did not inhibit microbial growth.

3. Permanganate treatment is ineffective as the chemical is not soluble in oil and favors an aqueous environment for oxidation.

4. Oil degradation occurred in all reactors based on observed heat release, weight loss and gas chromatograms of the recovered oil.

5. Oil degradation appeared to attack the saturate molecules in sludge from conventional oil refining. With heavy oils the more complex molecules appeared to be attacked.

6. Oil extraction was variable but oil loss in the reactors was 34%, 55% and 38% for conventional oil sludge and two heavy oil sludges respectively. Heavy oil sludge treated with 0.75 moles permanganate/Kg was degraded by 46%.

7. Oil loss in the reactors is due to a combination of air stripping of the volatiles and to microbial degradation.

8. Leachates from the reactors contained low levels of PAH's which may indicate microbial action on these molecules.

9. Only trace amounts of PAH's were found in the water traps on the reactors. Volatile PAH;s will not be retained by water traps..

10. Heavy metals were not found in the leachate from the reactors.

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7.0 RECOMMENDATIONS

1. The reactors should be allowed to run longer and results correlated with the composter at the Prince George refinery and the landfarm.

2. More careful analysis needs to be performed on the recovered oil to get a better handle on the percent degradation which is occurring.

3. Since 0.75 moles potassium permanganate/Kg sludge is ineffective after 24 hours at ambient temperature a more potent oxidizing treatment must be devised.

4. The levels of PAH's and heavy metals should be monitored in the sludges going into the reactors and in the recovered oil to determine their fate in the degradation process.

5. PAH degrading organisms should be enumerated in the reactors to obtain a correlation between their presence and the degradation of these compounds.

6. These reactors were set up without controls containing sludge but no microflora to determine the true effect of air stripping on the system. Adequate controls should be included in future studies.

7. Larger reactors should be built at Husky's Lloydminster refinery to study the degradation of a variety sludges from heavy crudes and determine how the reactors will perform in a field setting. Tank bottoms and API separator sludges should be used.

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9.0 TABLES

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TABLE 1: POLYAROMATIC HYDROCARBONS IN REACTOR 1 LEACHATE

PAH	CONCENTRATION (μg/L)		
	Week 4	Week 6	Week 10
Naphthalene	-	5.8	1.1
2-Methylnaphthalene	5.2	190	4.0
Acenaphthene	-	69	-
Dibenzofuran		-50	-
Fluorene	-	210	-
Phenanthrene	5	140	0.8
Anthracene	-	25	-
Pyrene	-	24	-
Chrysene/triphenylene	-	55	-

TABLE 2: METALS IN LEACHATE FROM REACTOR 1

METAL	CONCENTRATION (mg/L)
	6 Weeks
Cadmium	<0.002
Chromium	0.026
Lead	<0.03
Nickel	<0.01
Titanium	<0.002
Vanadium	<0.005
Zinc	0.02
Calcium	4.2
Magnesium	5.0
Manganese	0.38
Potassium	910
Phosphorous	890
Sodium	220

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TABLE 3: POLYAROMATIC HYDROCARBONS IN REACTOR 2 LEACHATE

PAH	CONCENTRATION (μg/L)	
	Week 2	Week 6
Naphthalene	0.6	-
2-Methylnaphthalene	0.8	2.3
Phenanthrene	1.3	5.7
Pyrene	-	3.2
Chrysene	-	2.3

TABLE 4: METALS IN LEACHATE FROM REACTOR 2

METAL	CONCENTRATION (mg/L)	
	2 Weeks	6 Weeks
Cadmium	<0.002	<0.002
Chromium	0.13	0.042
Lead	<0.03	<0.03
Nickel	<0.01	<0.01
Vanadium	<0.005	<0.005
Zinc	0.09	<0.01
Calcium	43	7.6
Magnesium	55	11
Manganese	4.4	0.70
Potassium	3500	1400
Phosphorous	3700	1400
Sodium	750	310

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TABLE 5: POLYAROMATIC HYDROCARBONS IN REACTOR 3 LEACHATE

	CONCENTRATION (μg/L)	
PAH	**Week 2**	**Week 6**
Naphthalene	1.3	-
2-Methylnaphthalene	1.3	-
Phenanthrene	-	-
Pyrene	-	-
Chrysene	-	-

TABLE 6: METALS IN LEACHATE FROM REACTOR 3

METAL	**CONCENTRATION (mg/L)**	
	2 Weeks	**6 Weeks**
Cadmium	<0.002	<0.002
Chromium	0.11	0.053
Lead	<0.03	<0.03
Nickel	<0.01	<0.01
Vanadium	<0.005	<0.005
Zinc	0.07	<0.01
Calcium	42	11
Magnesium	53	18
Manganese	4.2	1.3
Potassium	3300	1900
Phosphorous	3400	1800
Sodium	590	350

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TABLE 7A: OIL LOSS IN REACTOR 1 OVER SIX WEEK PERIOD

SAMPLING WEEK	OIL RECOVERED*					
	METHOD 1			METHOD 2		
	Oil + Solids	Oil	% Oil Loss	Oil + Solids	Oil	% Oil Loss
0	13.48	2.73	0	18.2	2.31	0
2	12.33	2.93	(+17)			
3	14.20	2.02	30			
6	13.72	3.03	(+9)	21.4	1.81	34

* Weight of oil and solids recovered is in grams. Values in brackets indicate more oil than present at the start and represent a gain in percentage of the oil. Percent oil loss is based on the oil recovered at week 0 as 100%.

Oil recovery at weeks 2 & 6 is suspect due to operator error.

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TABLE 7B: OIL LOSS IN REACTOR 2 OVER SIX WEEK PERIOD

SAMPLING WEEK	OIL RECOVERED*					
	METHOD 1			METHOD 2		
	Oil + Solids	Oil	% Oil Loss +	Oil + Solids	Oil	% Oil Loss
0	11.37	1.72	0	13.62	1.99	0
2	10.57	2.02	(+26)			
3	13.72	1.52	27			
6	11.28	1.58	7.3	21.76	1.42	55

* Weight of oil and solids recovered is in grams. Values in brackets indicate more oil than present at the start and represent a gain in percentage of the oil. Percent oil loss is based on the oil recovered at week 0 as 100%.

Oil recovery at weeks 2 & 6 is suspect due to operator error.

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TABLE 7C: OIL LOSS IN REACTOR 3 OVER SIX WEEK PERIOD

SAMPLING WEEK	OIL RECOVERED*					
	METHOD 1			METHOD 2		
	Oil + Solids	Oil	% Oil Loss	Oil + Solids	Oil	% Oil Loss
0	11.13	1.59	0	19.17	1.70	0
2	10.05	1.82	(+27)			
3	14.13	1.47	27			
6	11.26	1.60	1	23.82	1.32	38

* Weight of oil and solids recovered is in grams. Values in brackets indicate more oil than present at the start and represent a gain in percentage of the oil. Percent oil loss is based on the oil recovered at week 0 as 100%.

Oil recovery at weeks 2 & 6 is suspect due to operator error.

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10.0 FIGURES

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FIGURE 1: A SCHEMATIC DRAWING OF THE COMPOST REACTOR

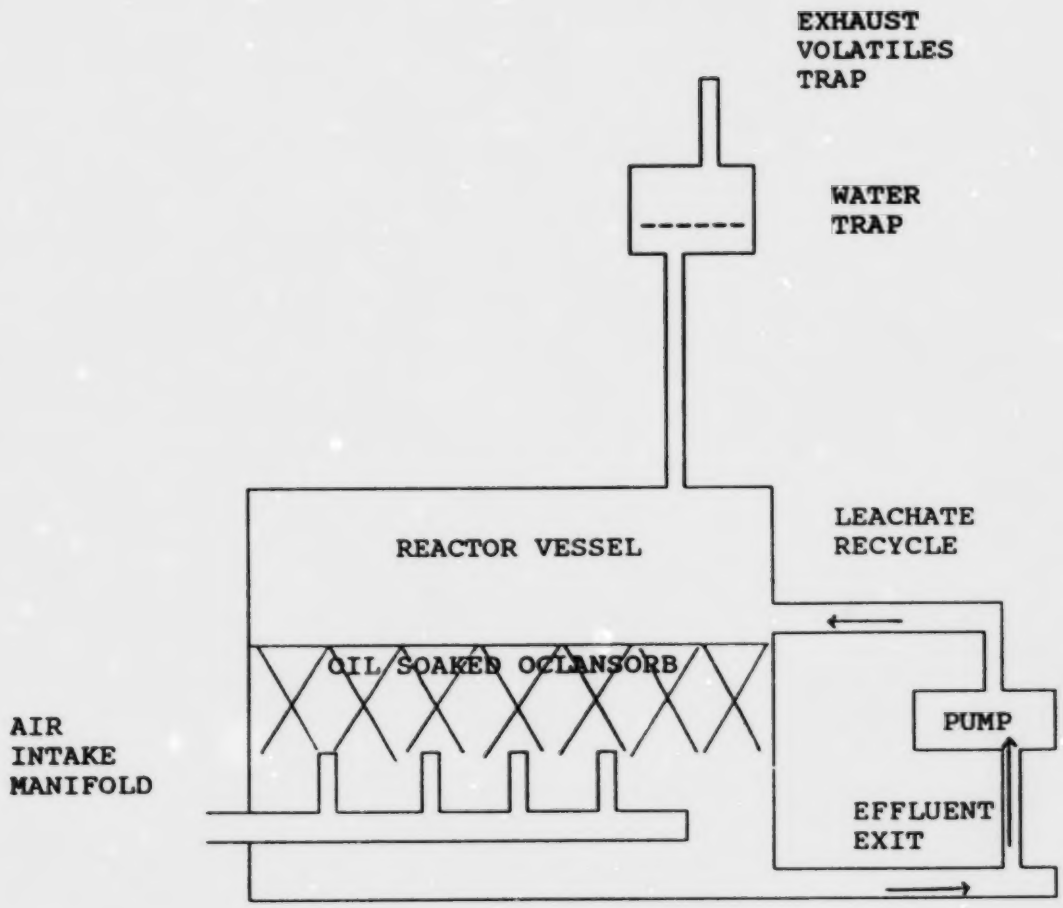

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FIGURE 2: REACTORS IN OPERATION AT NHRC

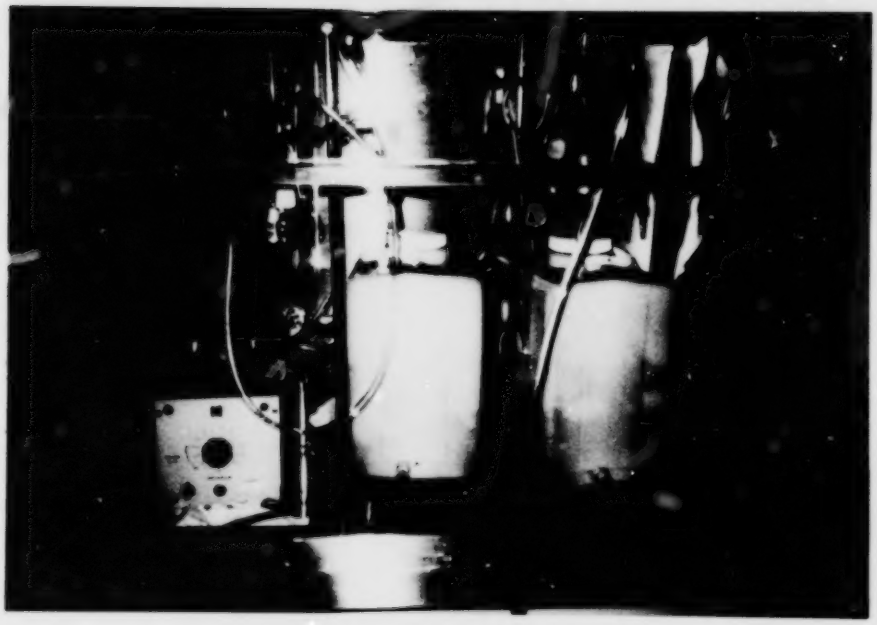

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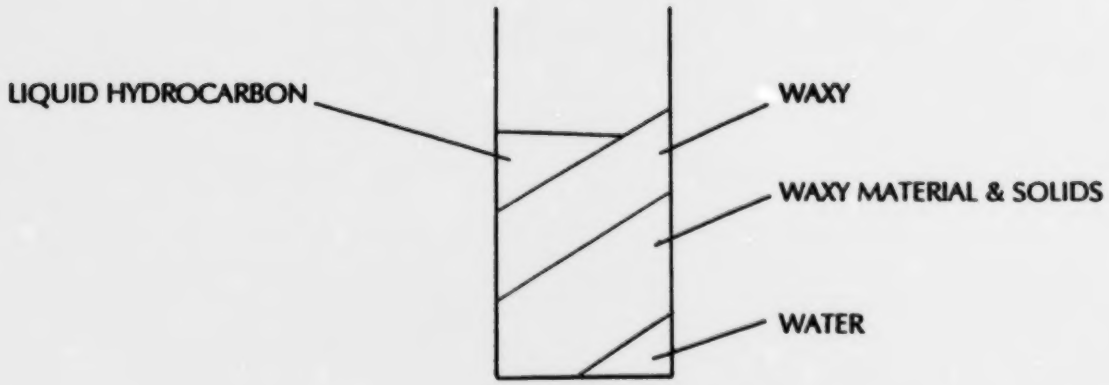
FIGURE 3: A SCHEMATIC OF SLUDGE FRACTIONATION BY CENTRIFUGATION



The waxy layer appeared to increase with increasing permanganate treatment.

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FIGURE 4: INFRARED SPECTRA OF SLUDGE BEFORE AND AFTER 0.75 moles/Kg PERMANGANATE TREATMENT

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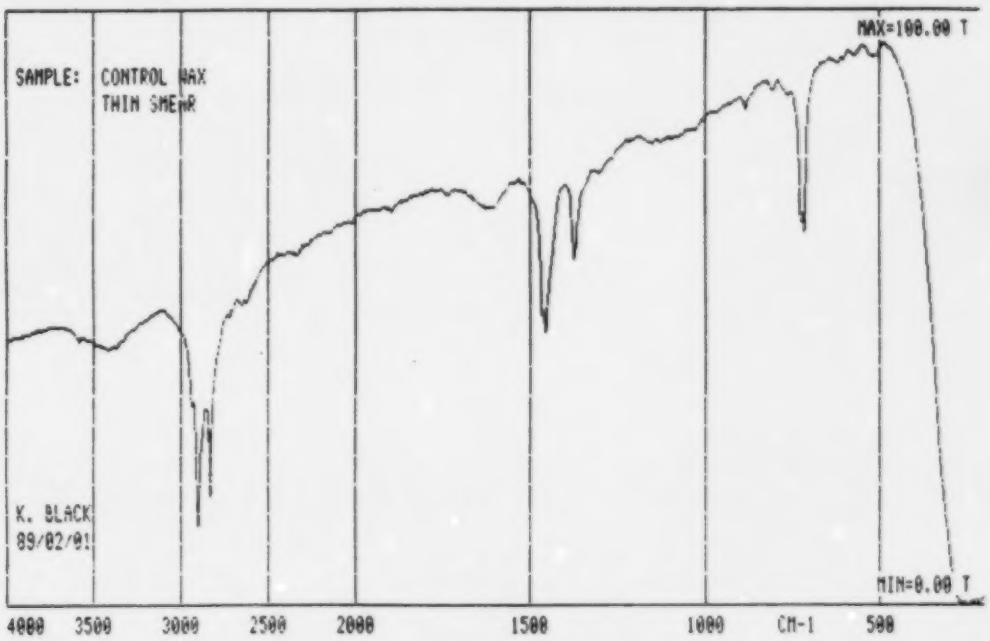
IR SPECTRUM OF 'CONTROL' SLUDGE - SOLID PORTION



IR SPECTRUM OF $KMnO_4$ - TREATED SLUDGE - SOLID PORTION

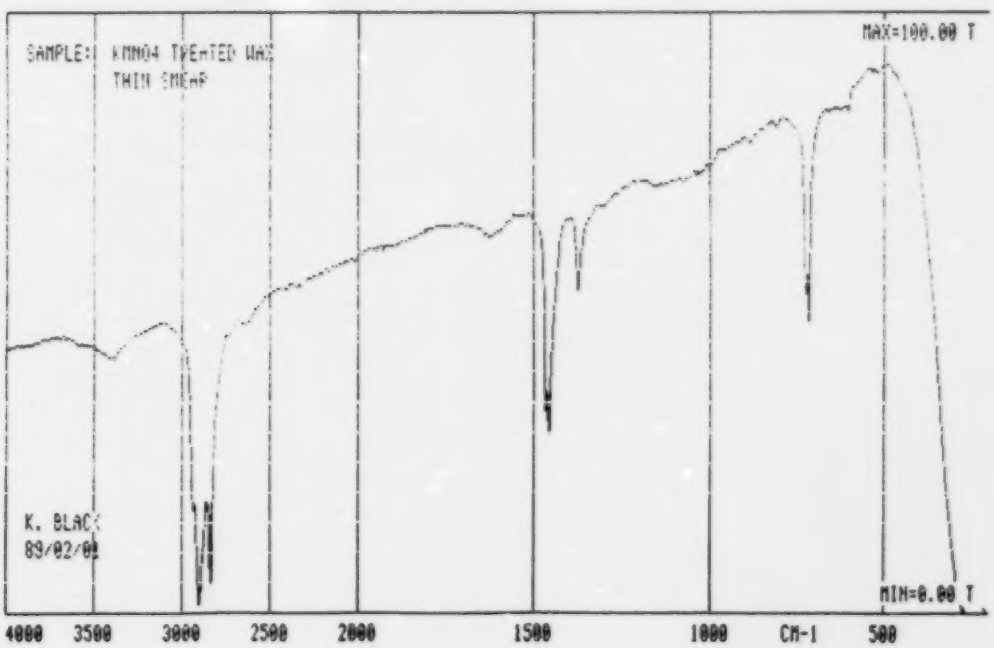


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FIGURE 5: GPC OF SLUDGE BEFORE AND AFTER 0.75 moles/Kg PERMANGANATE TREATMENT

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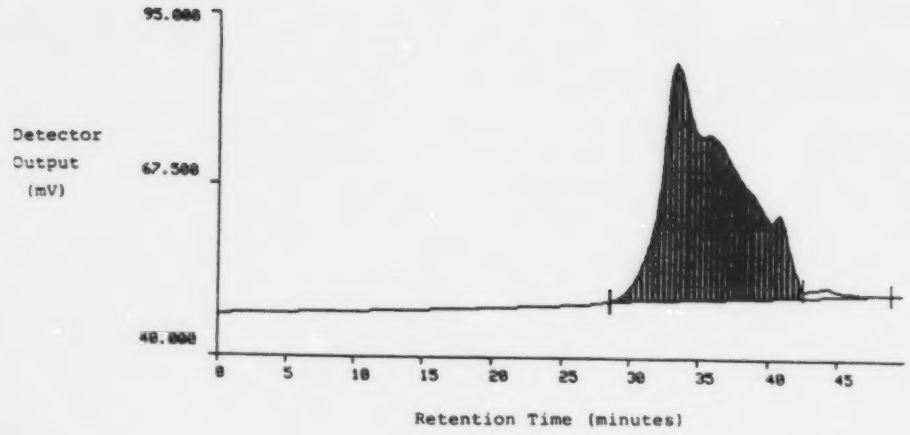
GPC Chromatogram of the Wax Layer of the Control Sample

Number Average	327
Weight Average	594
Z Average	907
Dispersivity	1.8



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GPC Chromatogram of the Wax Layer of the Sample Treated with Potassium Permanganate

Number Average	331
Weight Average	603
Z Average	918
Dispersivity	1.8

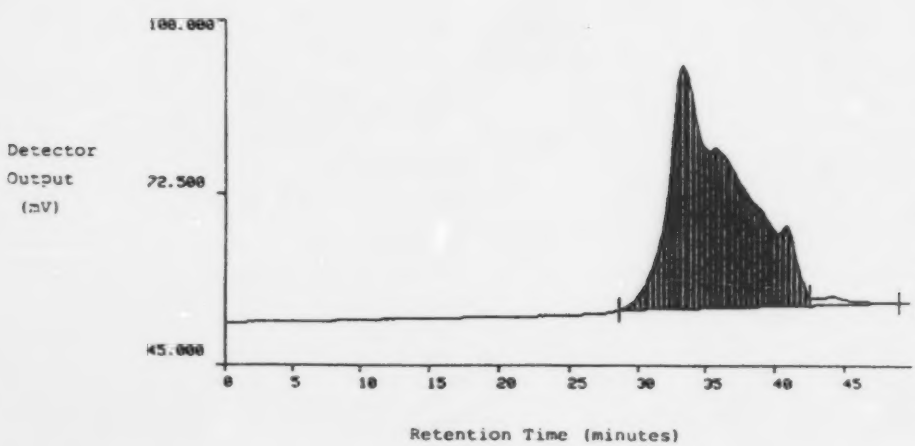

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FIGURE 6: CHANGES IN UV SPECTRA OF WATER FRACTION OF THE OIL AFTER PERMANGANATE TREATMENT

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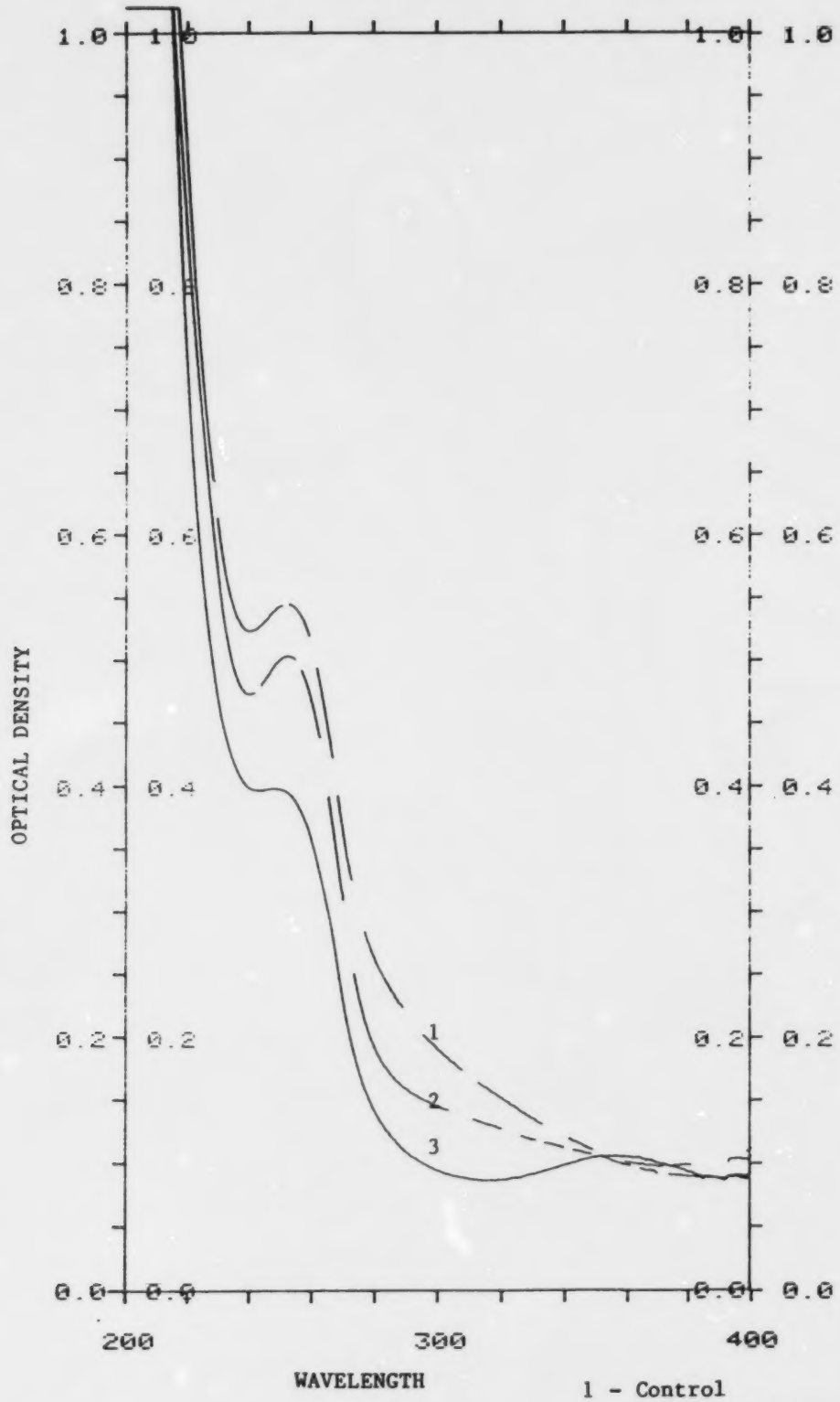

1 - Control
2 - 0.0075 moles $KMnO_4$/Kg
3 - 0.075 moles $KMnO_4$/Kg

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FIGURE 7: CHANGES IN UV SPECTRUM OF NAPHTHALENE AFTER PERMANGANATE TREATMENT

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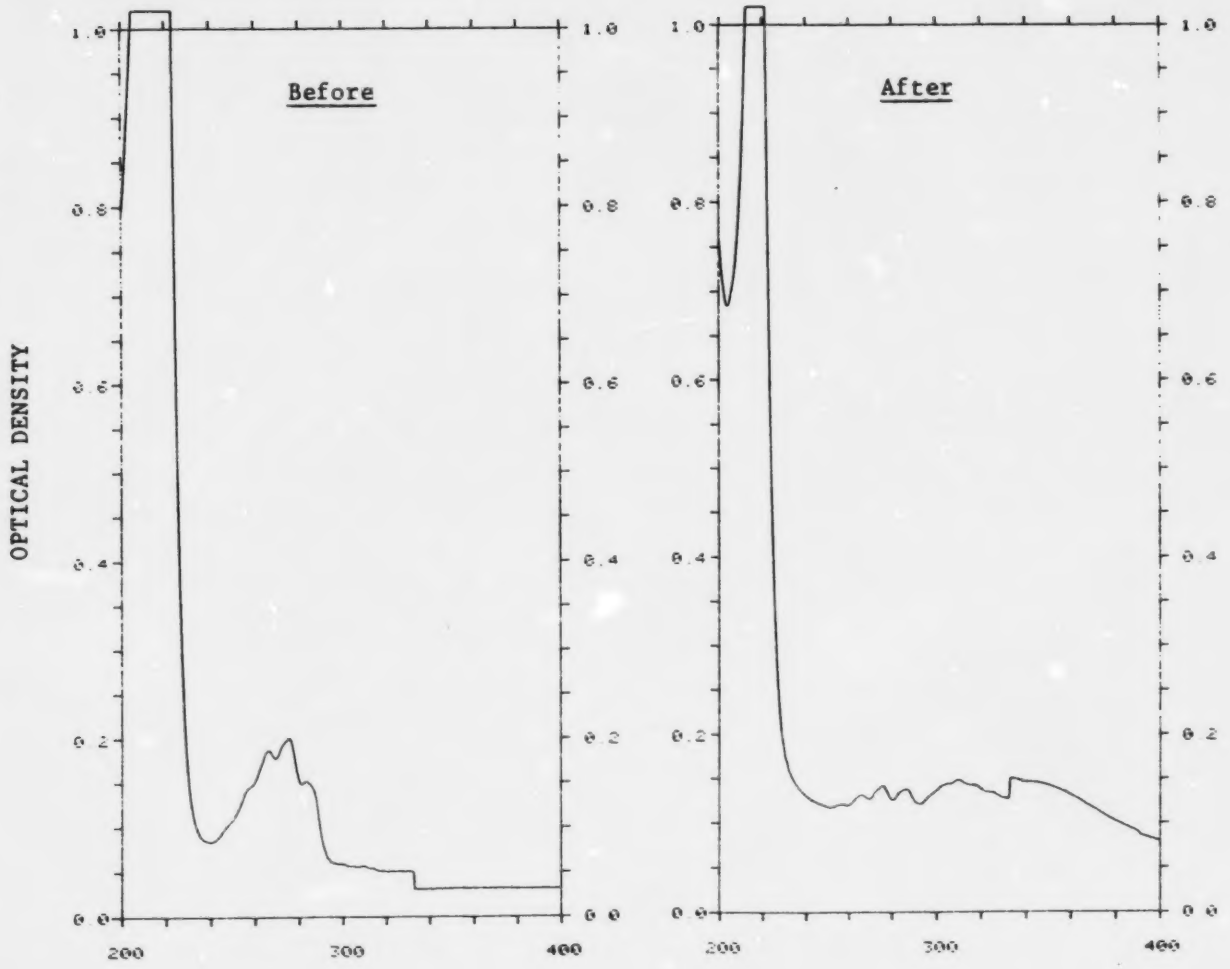

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FIGURE 8: CHANGES IN IR SPECTRUM OF DICHLOROMETHANE EXTRACTABLES IN WATER FRACTION OF OIL AFTER 0.75 moles/Kg PERMANGANATE TREATMENT

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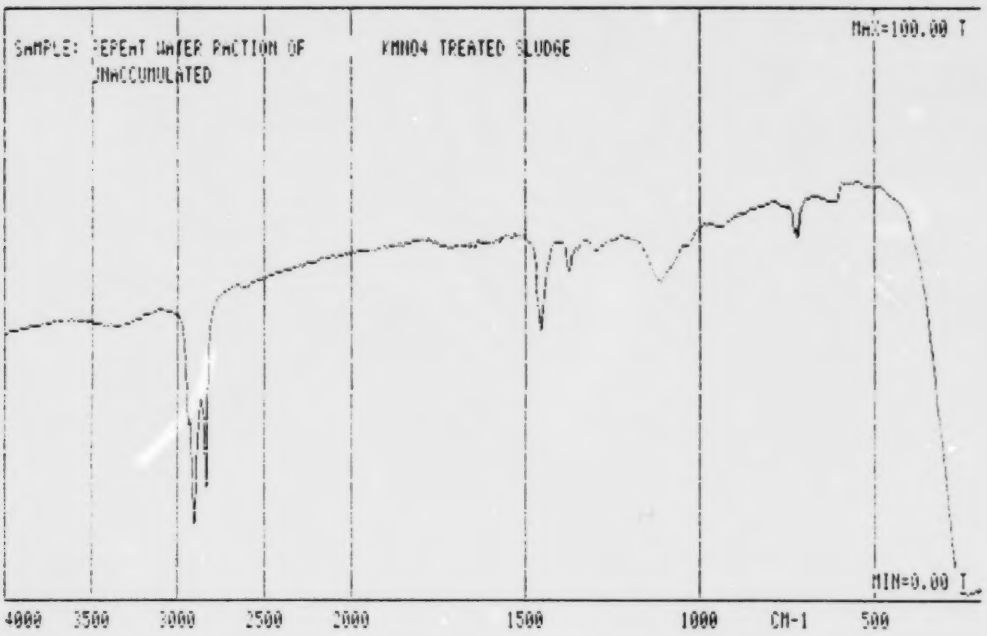
SAMPLE: REPEAT WATER FRACTION OF KMNO4 TREATED SLUDGE
UNACCUMULATED
MAX=100.00 T
MIN=0.00 T
4000 3500 3000 2500 2000 1500 1000 CM-1 500

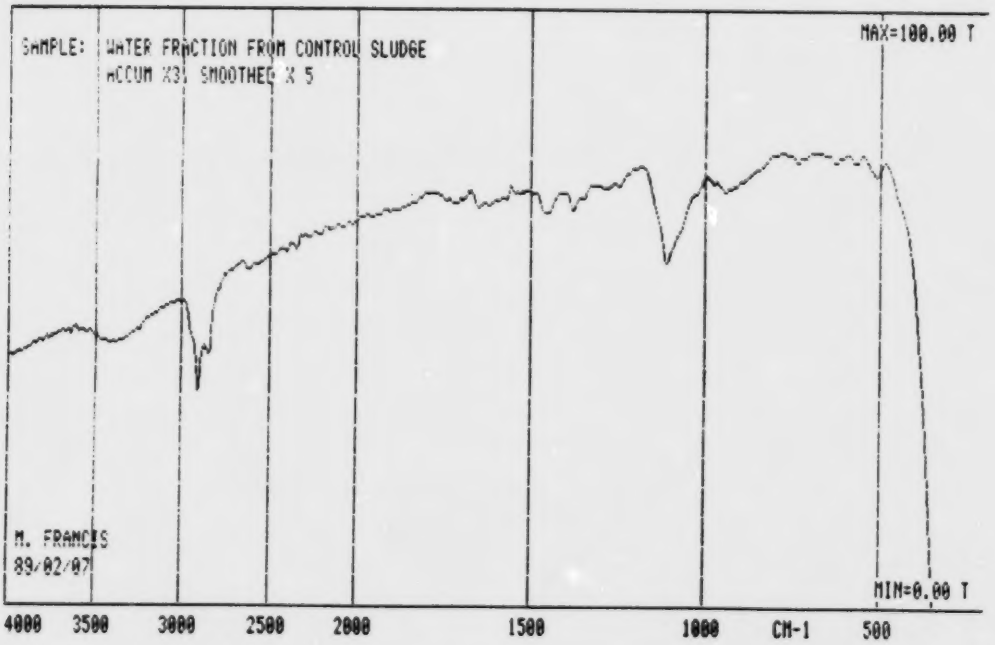

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FIGURE 9: REACTOR TEMPERATURES OVER THE COURSE OF THE STUDY

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TEMPERATURES IN REACTORS

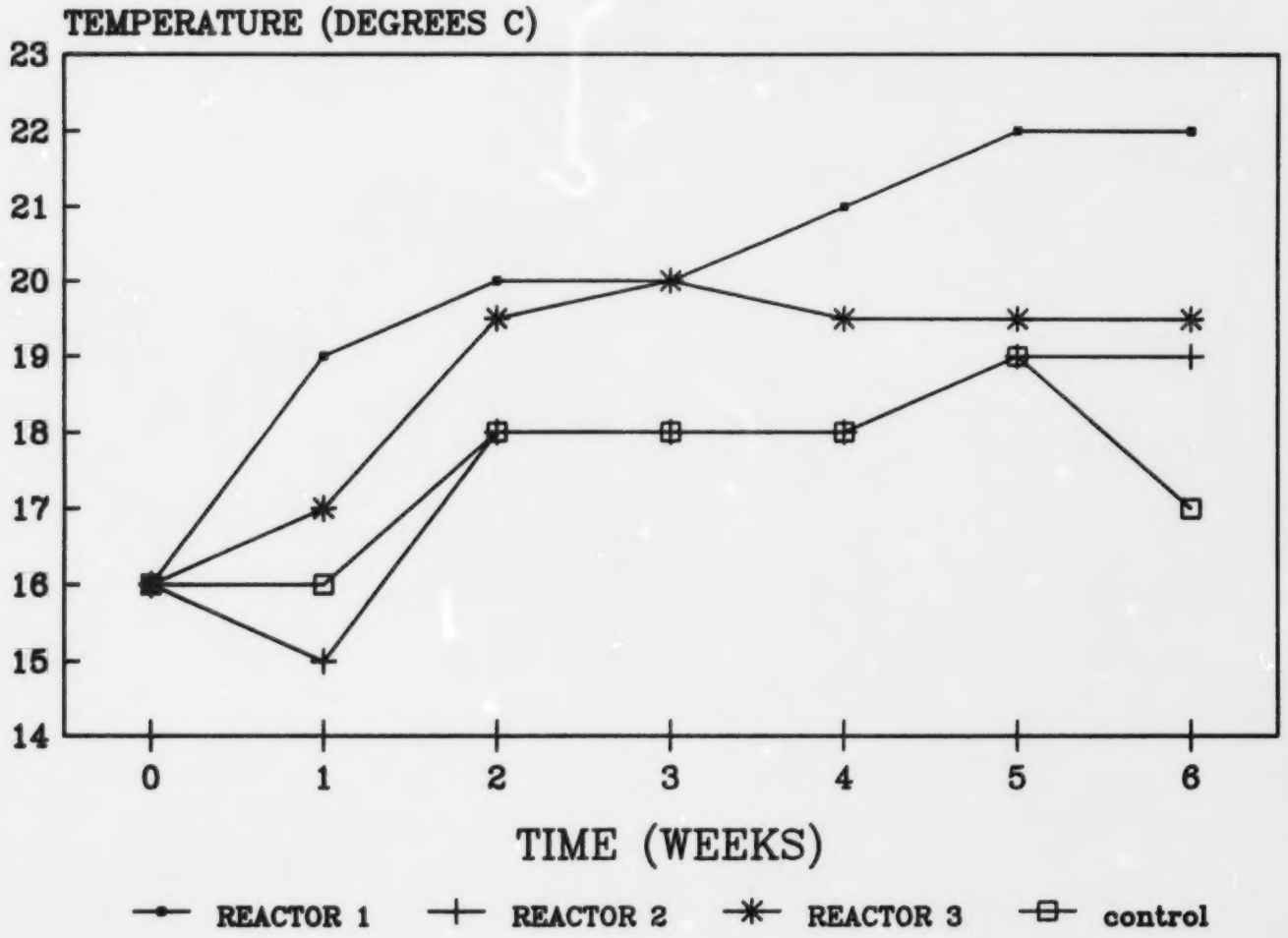

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FIGURE 10: GC PROFILES OF VOLATILE GASES FROM THE REACTORS OVER THE COURSE OF THE STUDY

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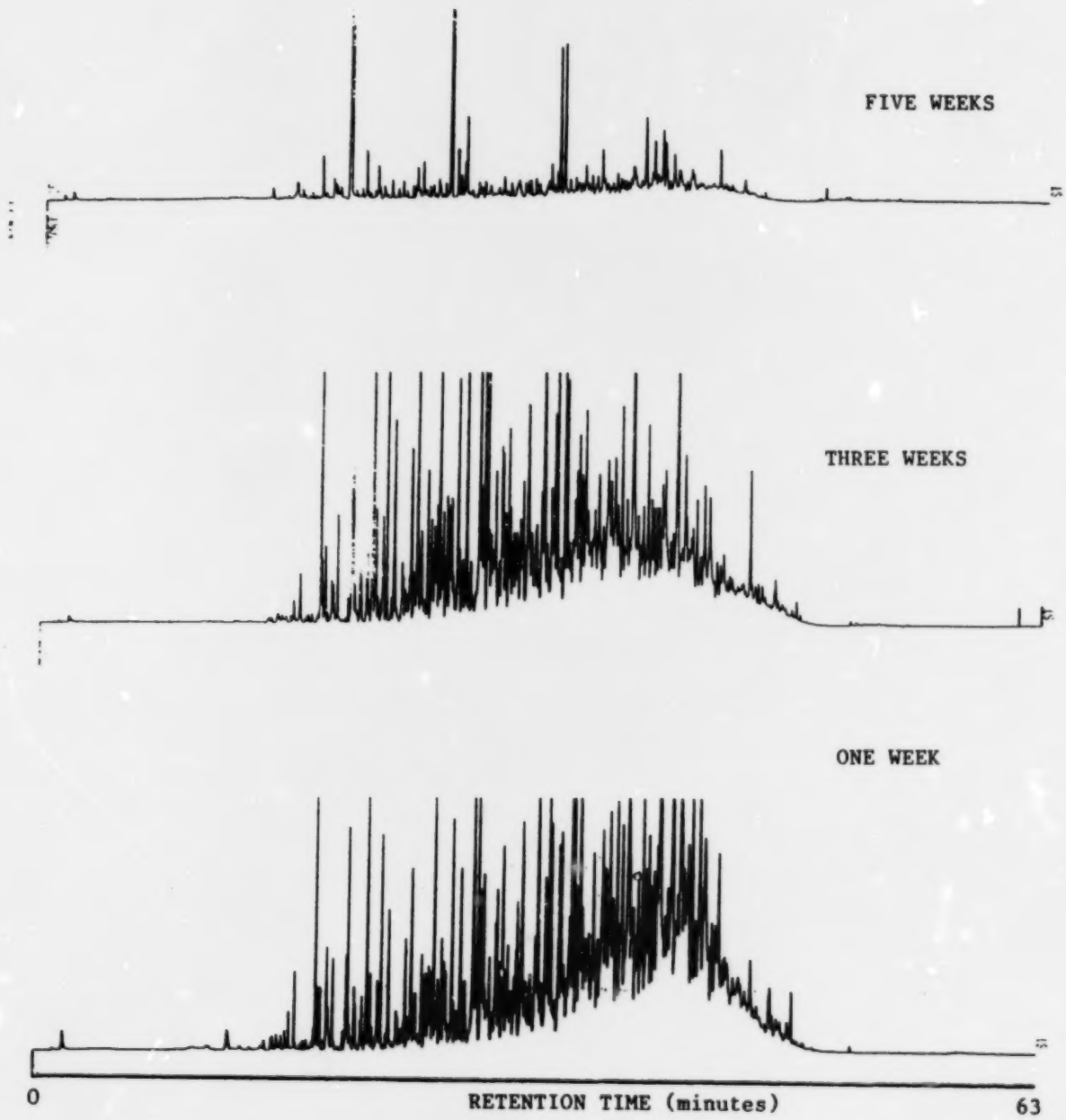
REACTOR 1



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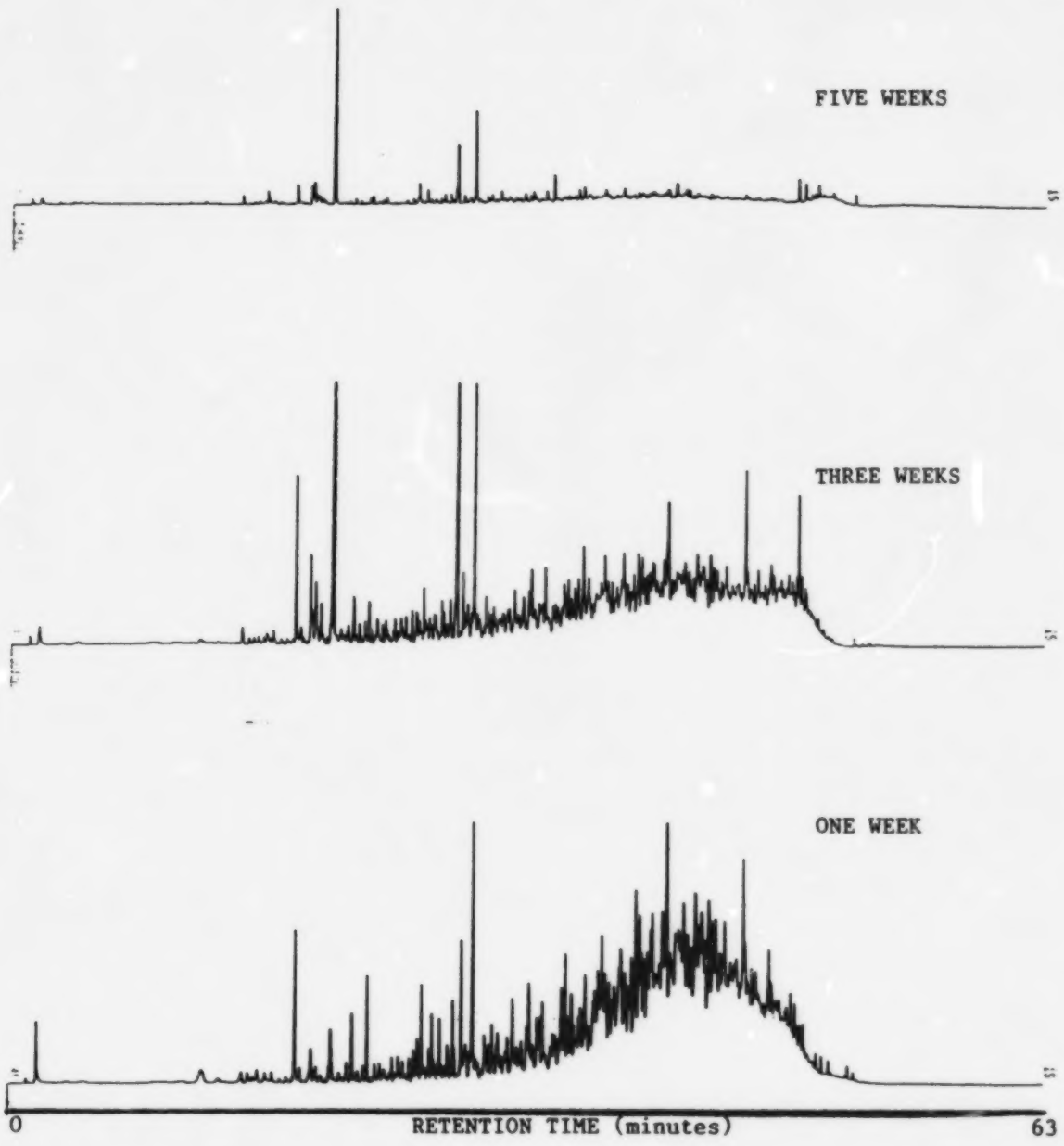
REACTOR 2



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REACTOR 3

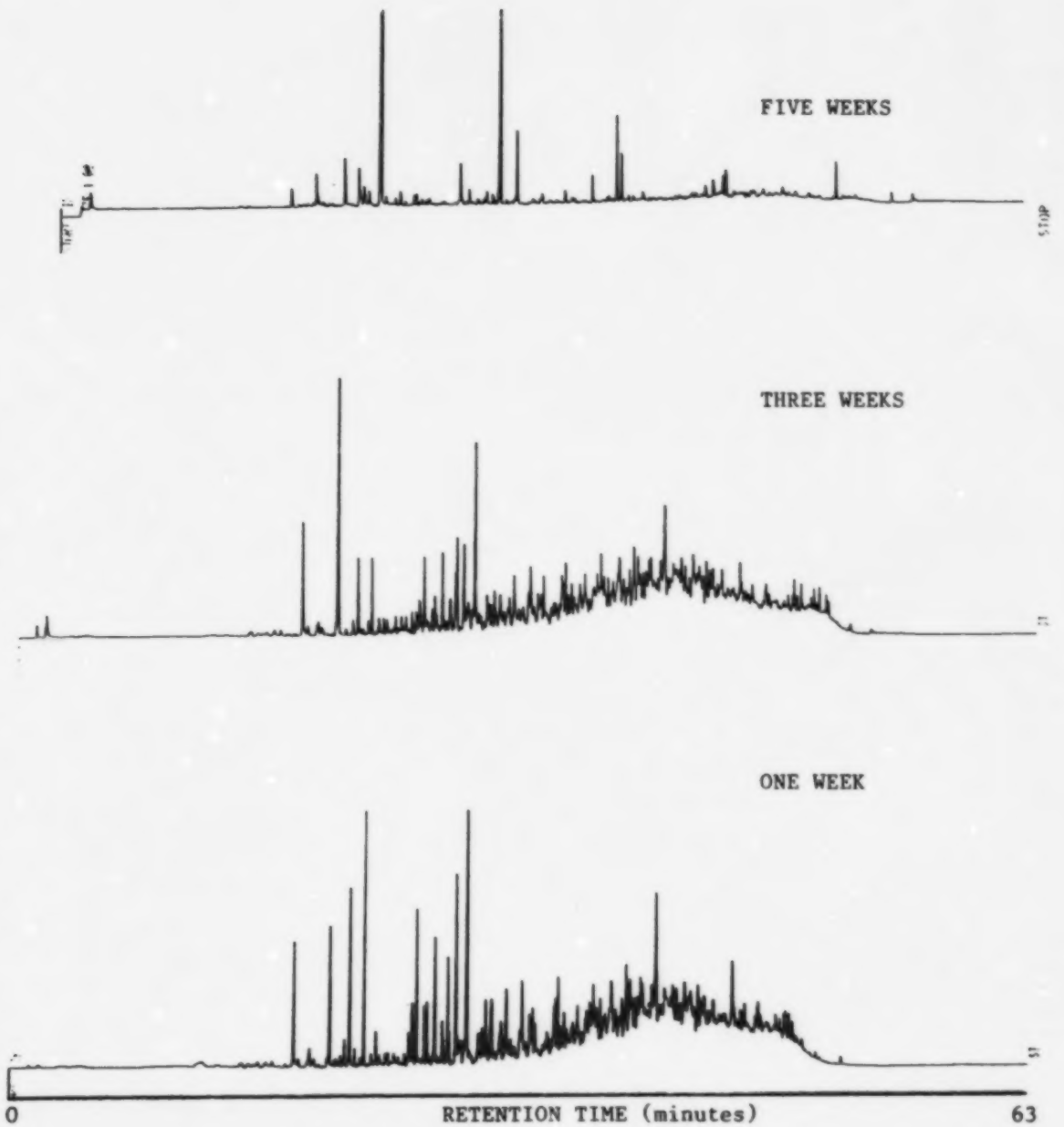

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FIGURE 11: PERCENT OIL LOSS IN REACTORS

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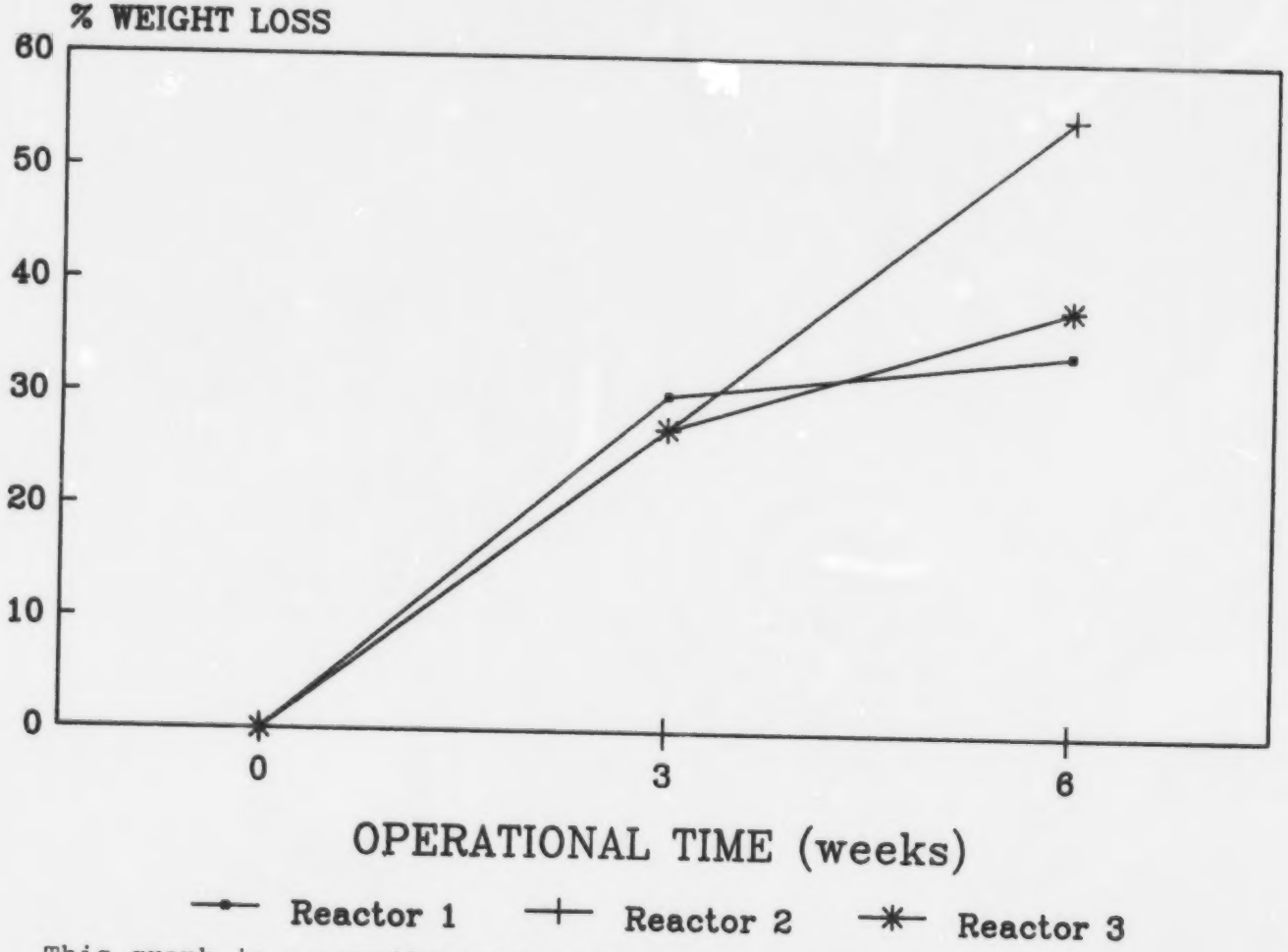
% WEIGHT LOSS IN REACTORS



This graph is a compilationof selected data from Table 7. It represents a trend only. There are no statistics available to test variance.

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FIGURE 12: CHANGING GC PATTERNS OF THE OIL IN REACTOR 1

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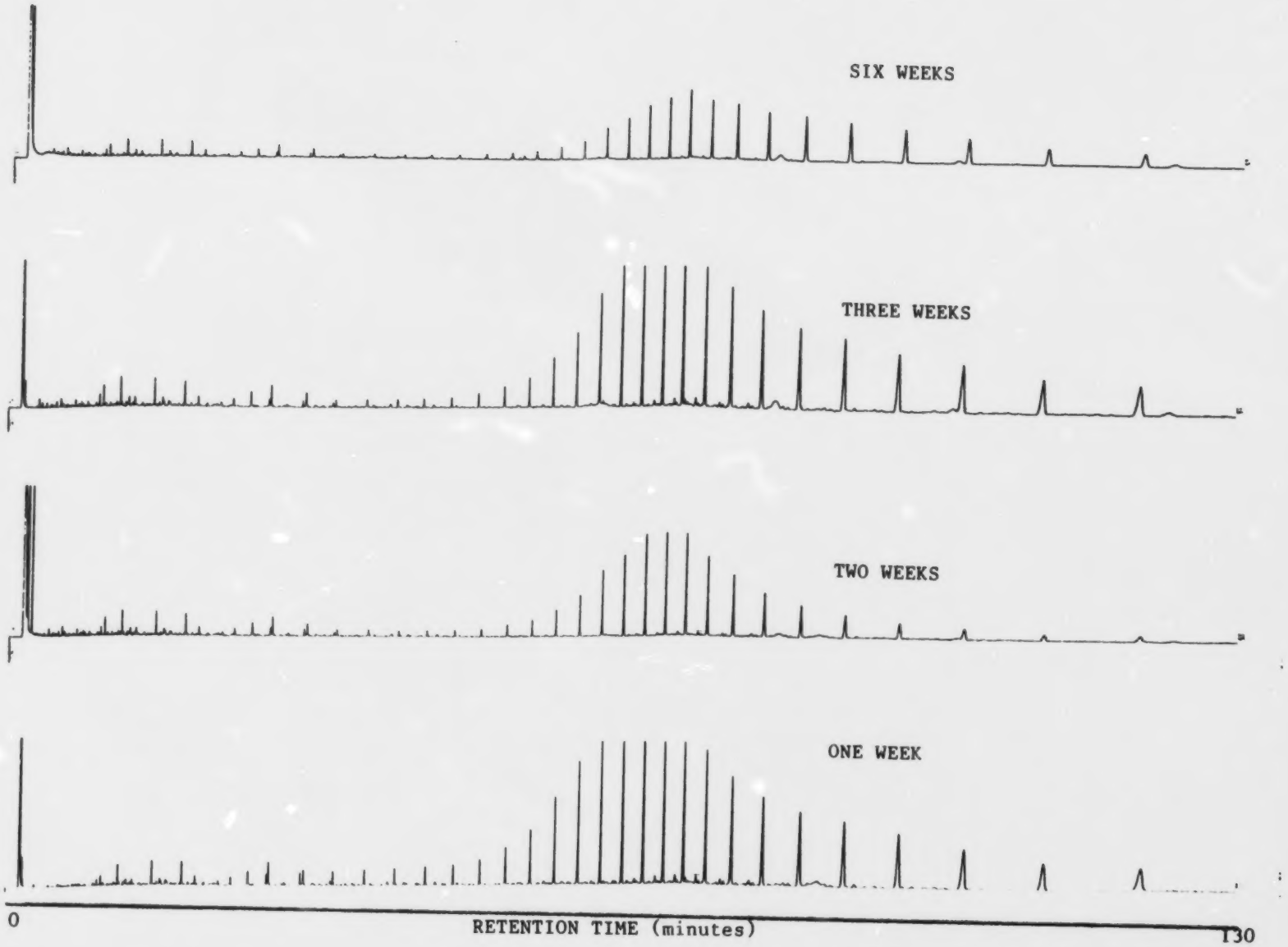

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FIGURE 13: GC PATTERN OF THE TOTAL OIL RECOVERED FROM REACTOR 2 OVER THE COURSE OF THE STUDY

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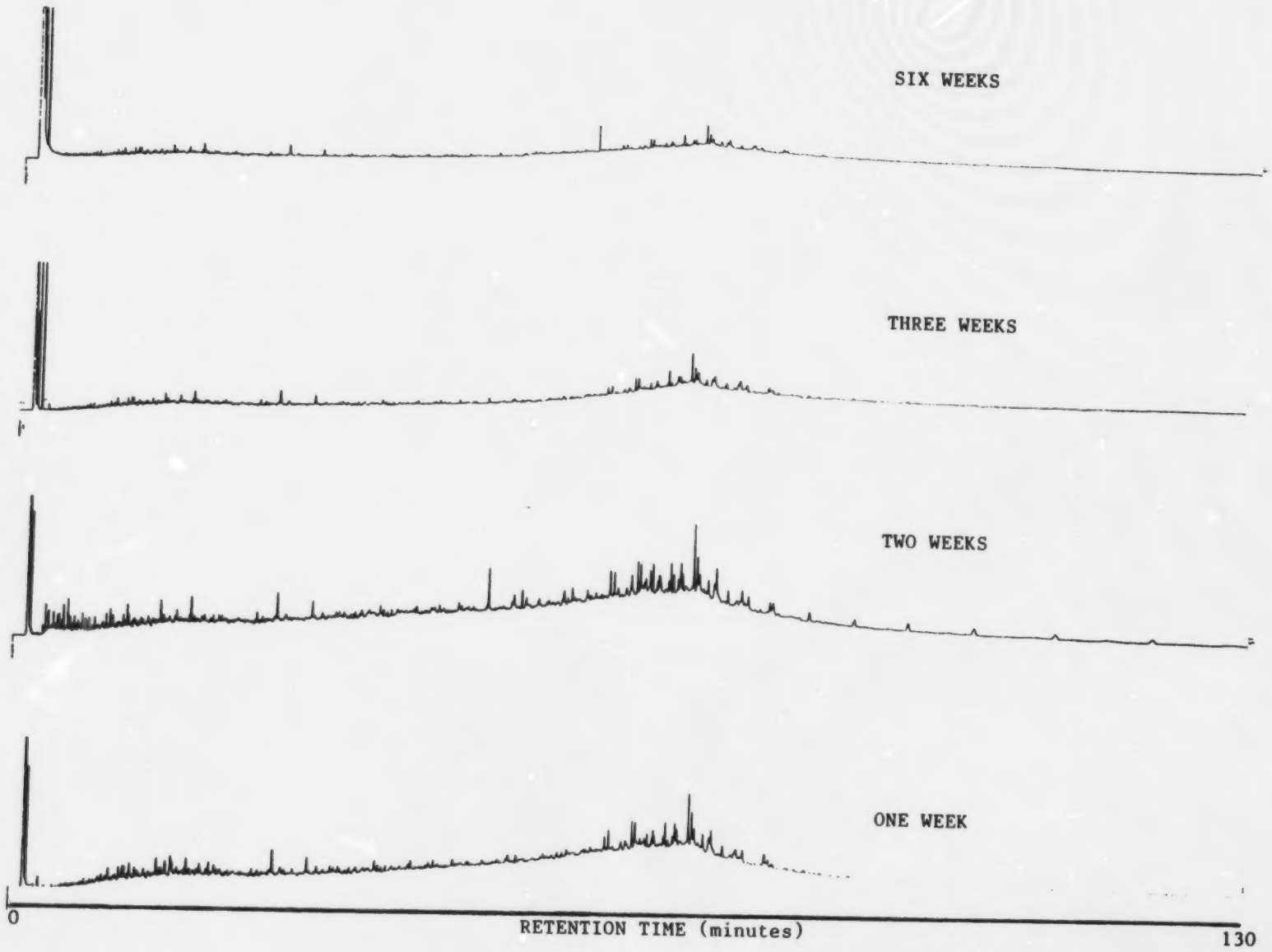

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FIGURE 14: CHANGING GC PATTERNS OF THE SATURATE FRACTION OF OIL RECOVERED FROM REACTOR 2 OVER THE COURSE OF THE STUDY

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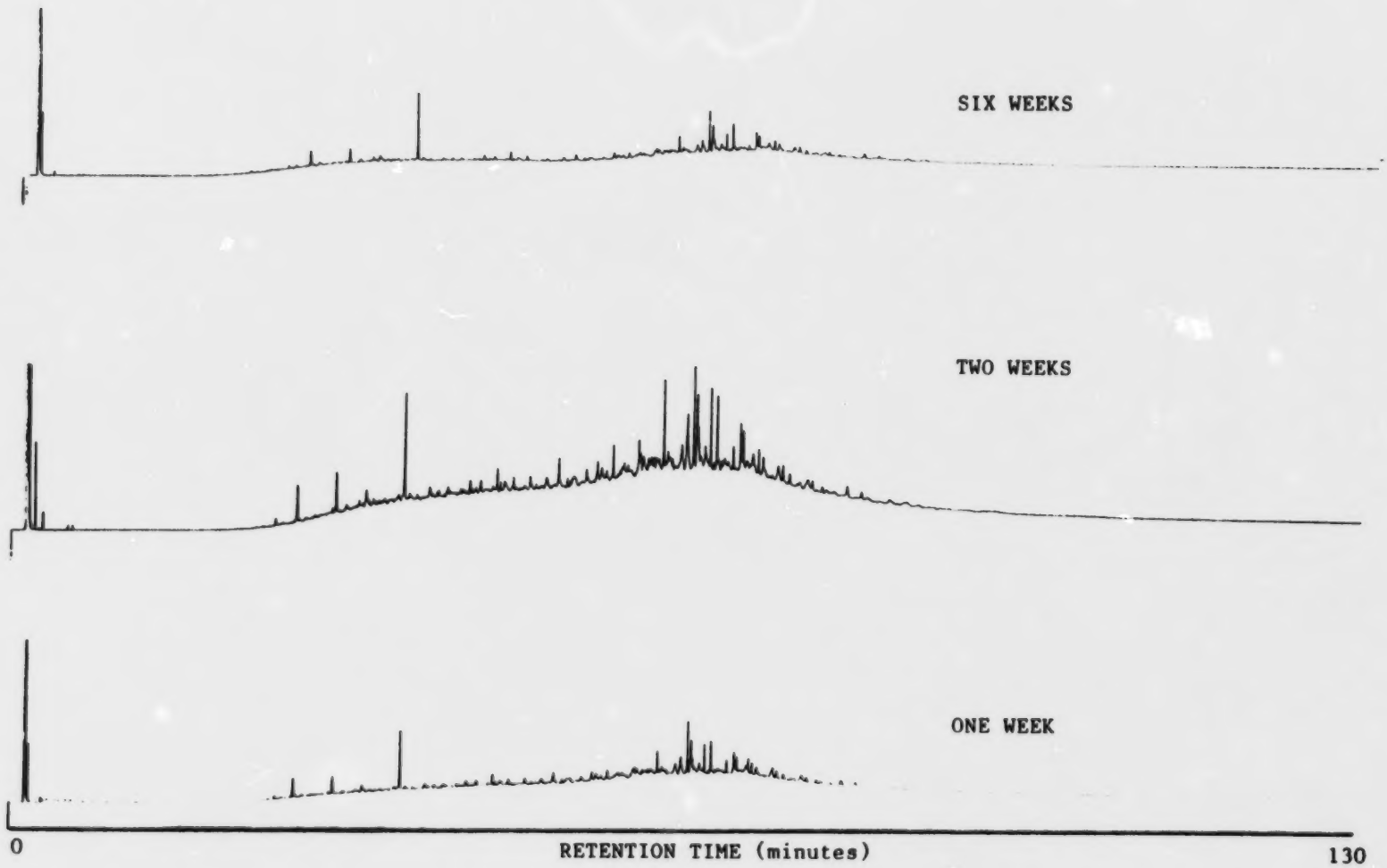

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FIGURE 15: CHANGING GC PATTERNS OF THE NAPHTHENE AROMATIC FRACTION OF THE OIL RECOVERED FROM REACTOR 2 OVER THE COURSE OF THE STUDY

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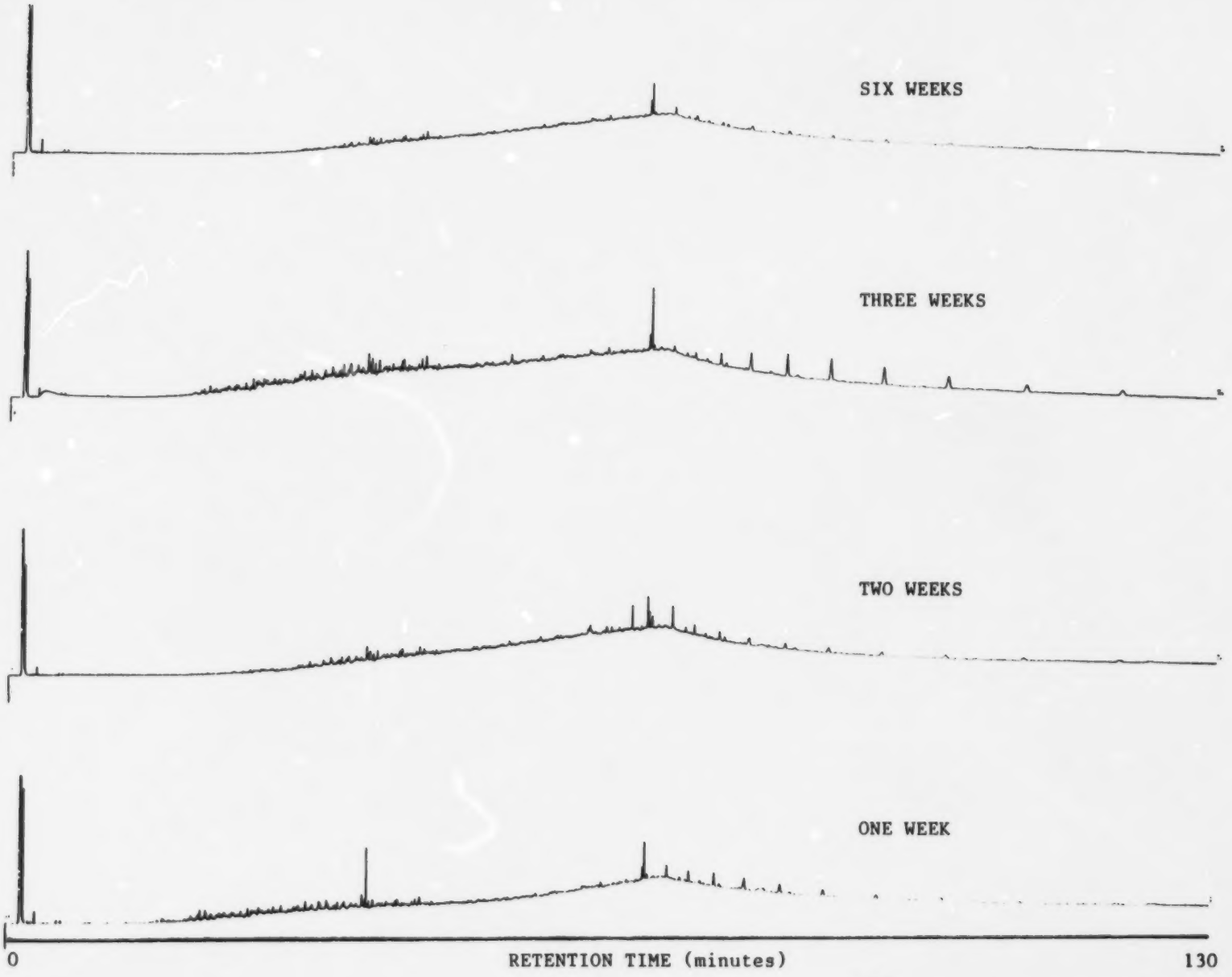

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FIGURE 16: GC PATTERNS OF THE TOTAL OIL RECOVERED FROM REACTOR 3 OVER THE COURSE OF THE STUDY

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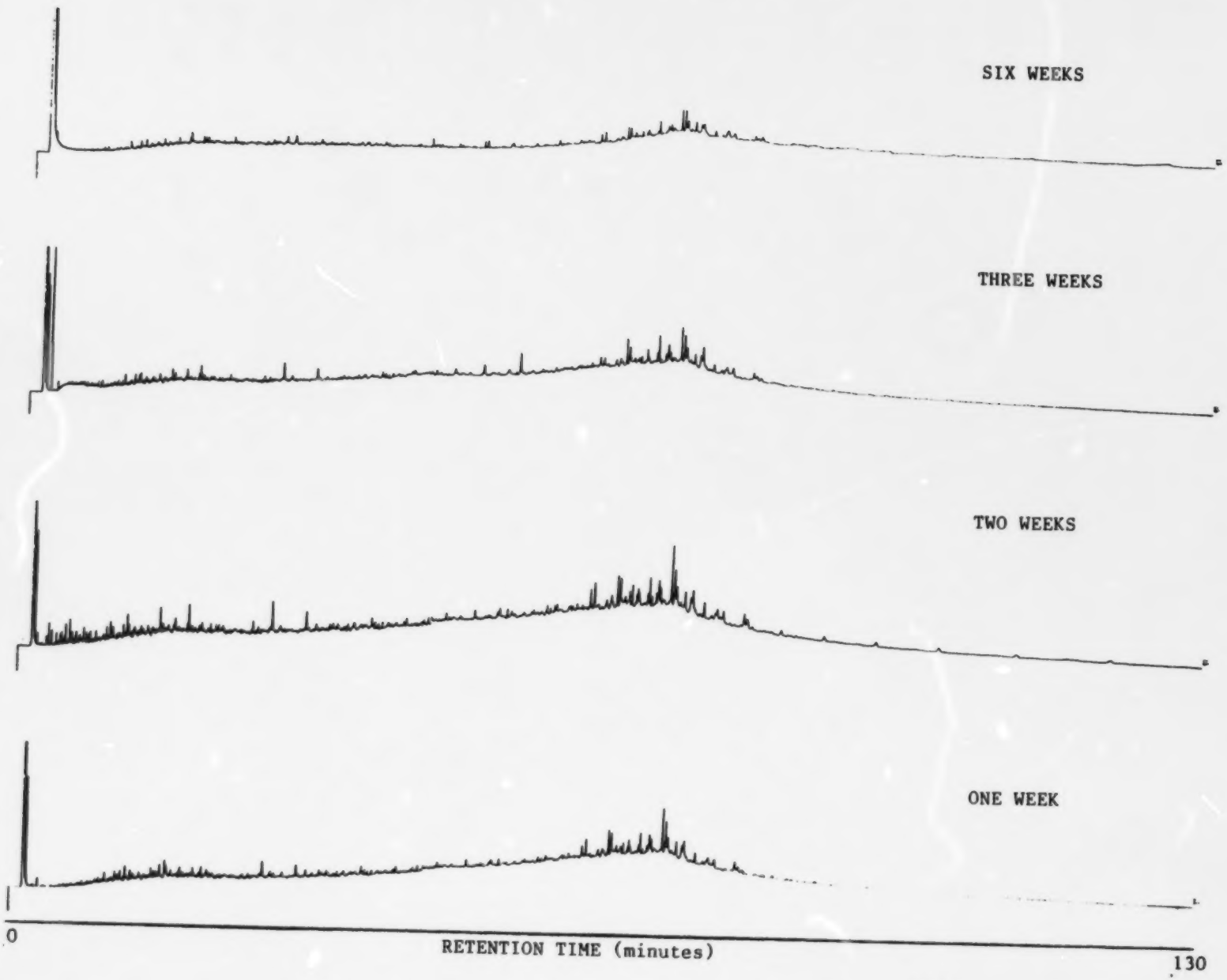

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FIGURE 17: GC PATTERNS OF SATURATE FRACTION OF THE OIL RECOVERED FROM REACTOR 3 OVER THE COURSE OF THE STUDY

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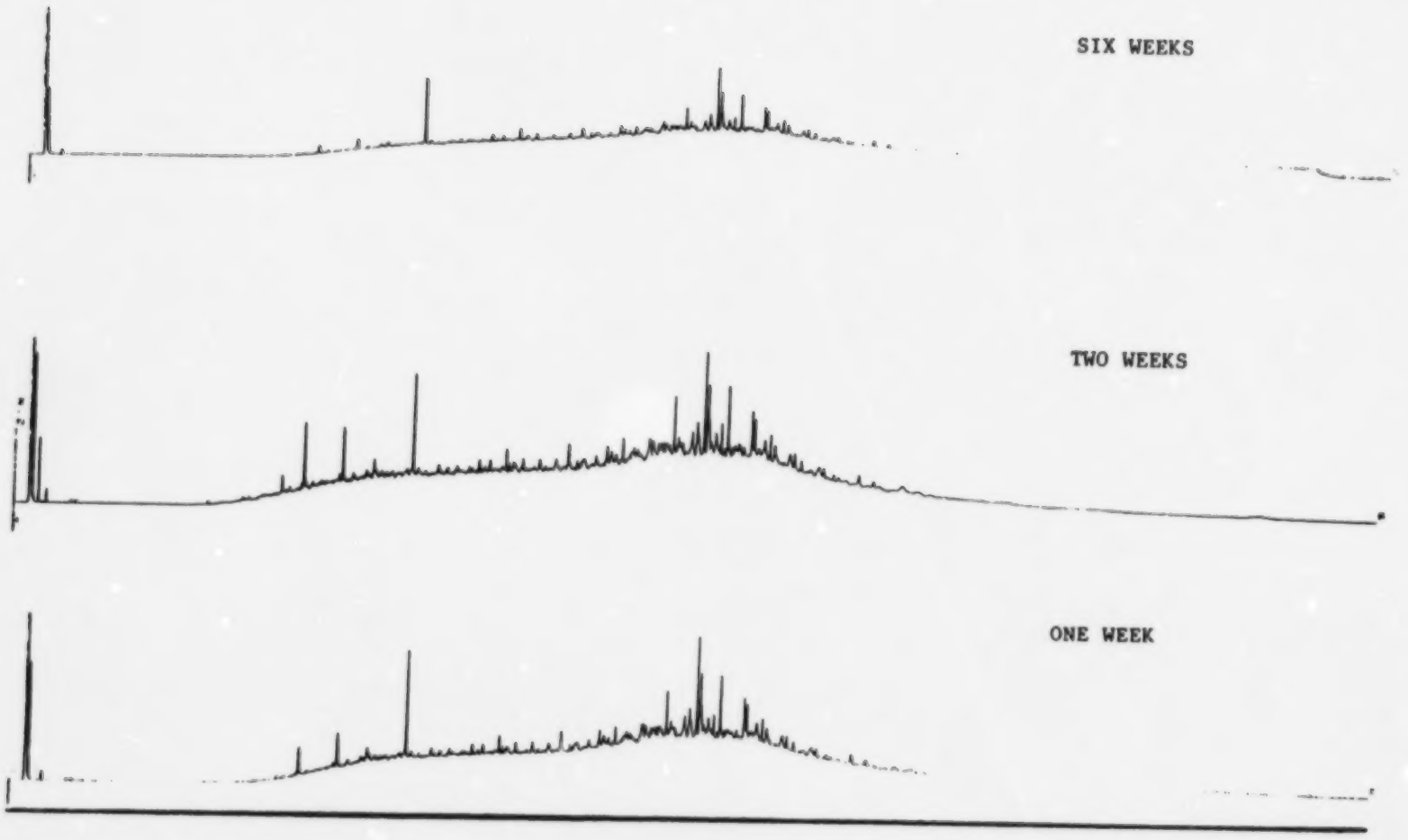

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FIGURE 18: GC PATTERNS OF THE NAPHTHENE AROMATIC FRACTION OF THE OIL RECOVERED FROM REACTOR 3 OVER THE COURSE OF THE STUDY

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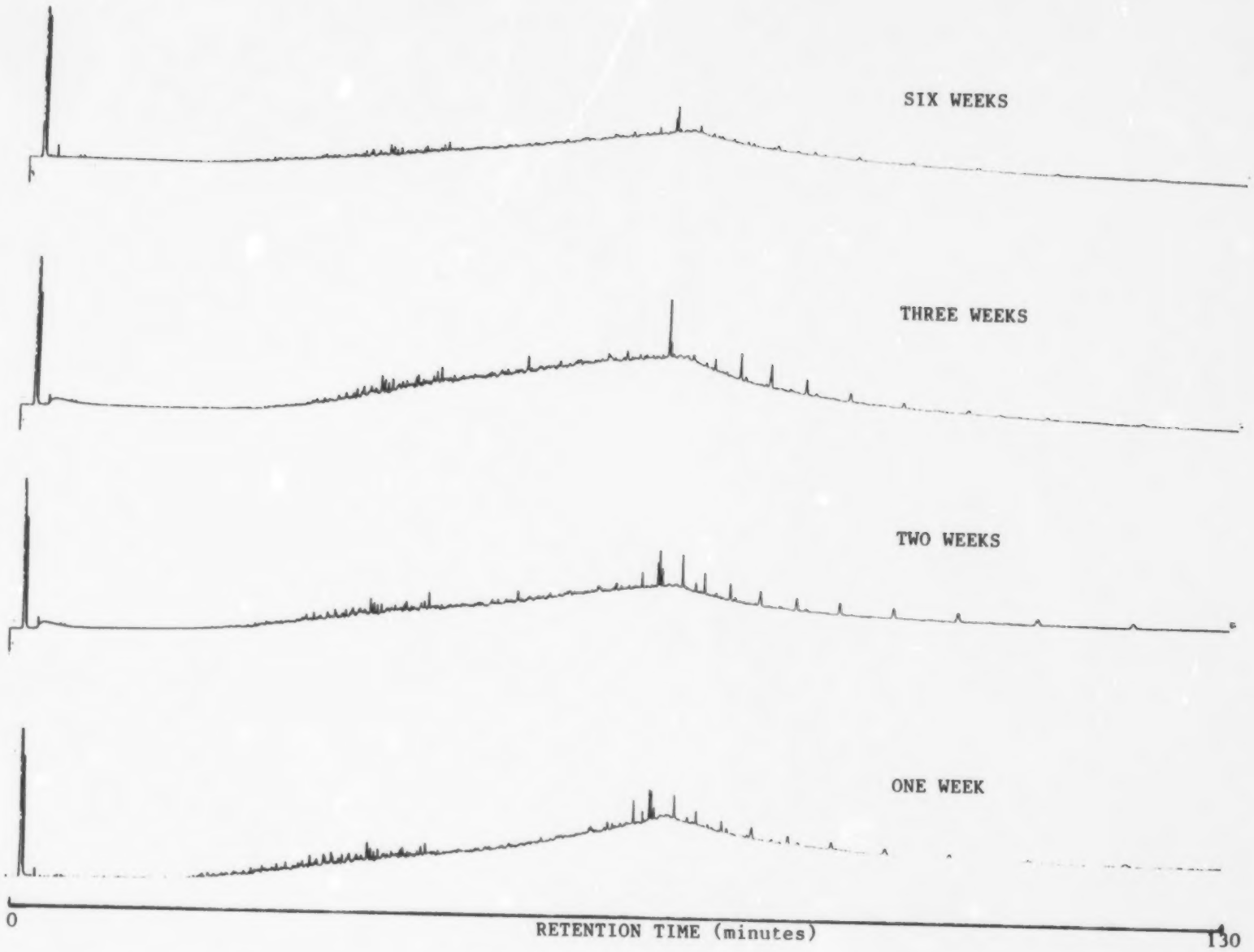

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FIGURE 19: GC PATTERNS OF THE OIL RECOVERED FROM SLUDGE TREATED WITH 0.75 MOLES/Kg POTASSIUM PERMANGANATE

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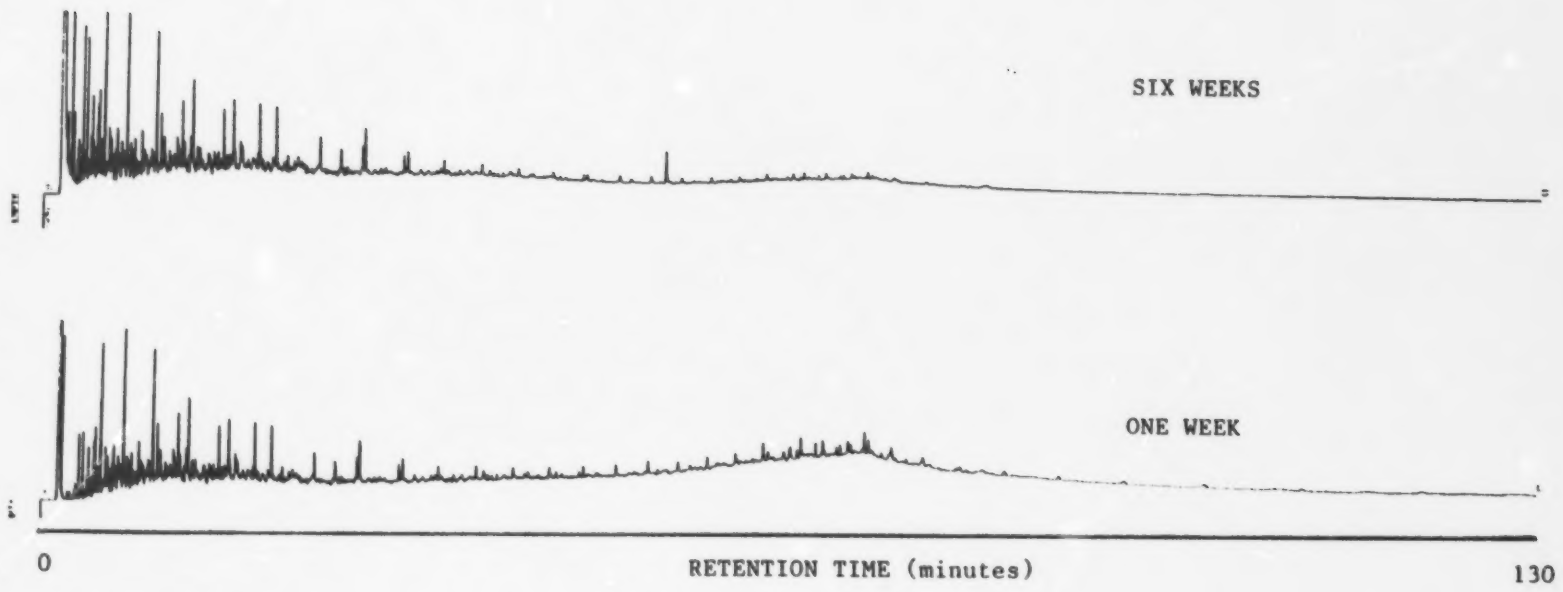

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FIGURE 20: BACTERIAL NUMBERS ON THE OCLANSORB AND IN THE WATER IN REACTOR 2 DURING THE COURSE OF THE EXPERIMENT

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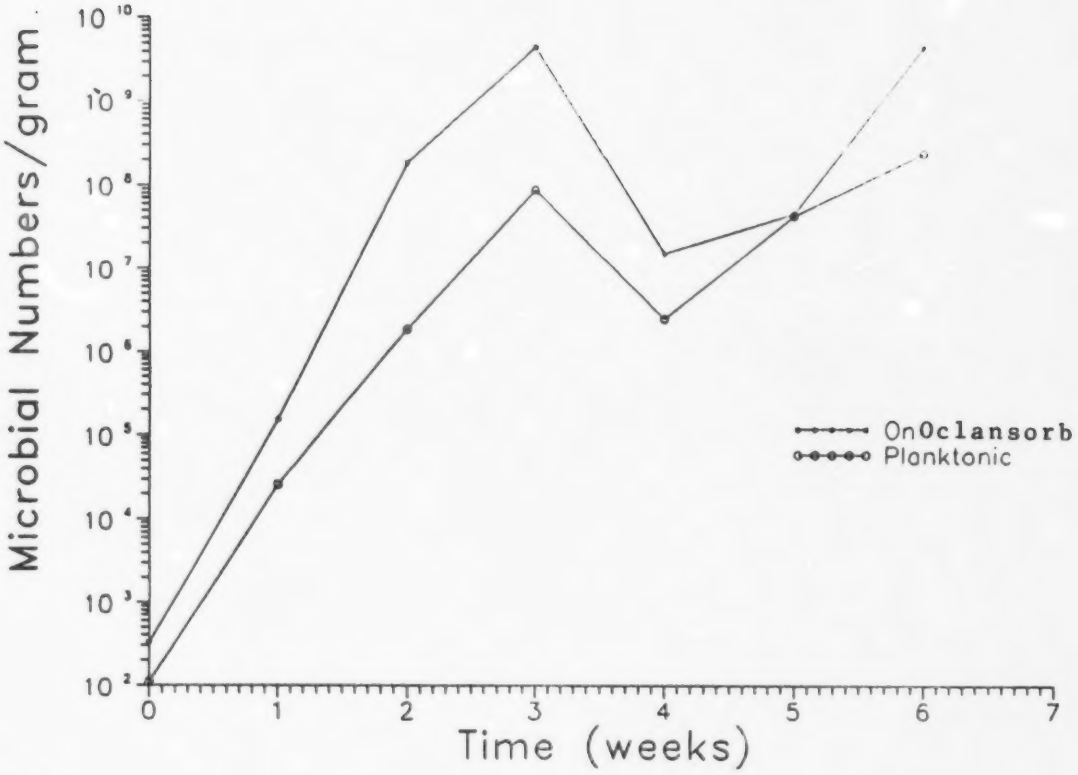

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APPENDIX A

THE DEAN STARK EXTRACTION PROCEDURE

SYNCRUDE
ANALYTICAL METHODS FOR OIL SAND
AND
BITUMEN PROCESSING

SYNCRUDE CANADA LIMITED
EDMONTON, ALBERTA, CANADA
August 1979

Determination of Bitumen, Water and Solids Content of Middlings and Tailings Samples (Classical)

Scope: This method determines the bitumen, water and solids content of middlings an tailings samples. Preferred sample sizes range from 250 to 600 g, although th method may be modified for smaller samples.

Summary: The sample is separated into bitumen, water and solids by refluxing with toluene in solids extraction apparatus. Condensed solvent and co-distilled water ar continuously separated in a trap. The water is drained from the lower portion of th trap while the solvent recycles through the extraction thimble to dissolve bitumen When the extraction is complete, the clean solids retained in the thimble are dried an weighed. A density measurement is employed to determine the bitumen content o the extract. Water is determined by difference.

Safety Considerations:

1. Hydrochloric acid — highly toxic by inhalation. A strong irritant to eyes and skin
2. Toluene — moderately toxic by inhalation and skin absorption. Possesses irritant and anesthetic properties. Highly flammable.

Apparatus, Reagents, Materials:

1. Condenser — an indented tube condenser having a water jacket at leas 535 mm long with a 29/42 standard taper male joint at the base.
2. Water trap — constructed to continuously separate water and solvent. The tra portion, which is approximately 25 mm in diameter and 220 mm long, has volume of about 130 mL. The lower end is fitted with a stopcock for removal water while the upper section has a 29/42 standard taper female joint accommodate the condenser. The downcomer has a 103/60 standard tap male joint for connection to the kettle and is perforated with 3 mm diamet holes below the ground glass.
3. Kettle — a heat-resistant glass vessel having a capacity of 2000 mL. The nec has a minimum length of 390 mm and includes a 103/60 standard taper fema joint.
4. Extraction thimble — Whatman 85 x 200 mm cellulose thimble, single thickness
5. Thimble basket — a corrosion-resistant basket to support the thimble. Se Figure 1. Fabrication from 3 mm diameter nichrome wire using a silver solde bottom joint is suitable.
6. Solvent distributor — corrosion-resistant, as shown in Figure 2.
7. Heating mantle — 500 W, to accommodate 2000 mL kettle.

The assembled extraction apparatus is shown schematically in Figure 3. If sample are less than 100 g, then the extraction apparatus described in Method 2.7 is used with the exception that the lower end of the water trap is fitted with a drain coc Volumes employed in the following procedure are then gauged accordingly.

8. Kimwipes — Type 1300.
9. Supply of 800 mL beakers.
10. Volumetric flasks — 250 and 1000 mL, Class A.
11. Syringe — 5 mL, glass, Luer-Lok tip.
12. Disposable filter assemblies — Millipore Millex filters, 0.45 µm, 25 m diameter, catalogue no. SLHA 025 OS.
13. Densimeter — six place densimeter with constant temperature water bath f temperature control to ±0.01°C. The water bath is operated at 20°C.
14. Balances:
    Top loading balance to ±0.01 g, 1200 g capacity.
    Analytical balance.

15. Drying oven — forced draft, set at 120°C.
16. Desiccator.
17. Reagents:
    Hydrochloric acid. A.C.S. reagent grade.
    Toluene, A.C.S. reagent grade.
18. Distilled water.

Procedure: Sample Handling

1. Insert 3 Kimwipes into each of a quantity of thimbles. Place the thimbles into 800 mL beakers and weigh to the nearest 0.01 g.
2. Clean the outer walls of the sample container and lid. Weigh to the nearest 0.1 g. Carefully add 0.5 mL of concentrated hydrochloric acid to the sample. Then add approximately 100 mL of toluene and stir until all the bitumen adhering to the wall of the sample container is dissolved.
3. Remove the Kimwipes from the thimble, insert the thimble into a thimble basket and mount the basket by its support into the neck of a kettle. Add approximately 900 mL of toluene to the kettle by pouring it through the thimble.
4. Restir the sample and while it is still in motion transfer to the thimble. Wash the container with toluene to remove all the bitumen. Add the washings to the thimble. Transfer the bulk of the remaining solids by scraping with a spatula. Finally, rinse and transfer remaining solids with distilled water. Clean and dry the container and lid with the Kimwipes and place them in the thimble. Weigh the container and lid.

Extraction

5. Assemble the extraction apparatus as shown in Figure 3, ensure all joints are vapour tight, and begin refluxing. Drain and discard water from the trap when it nears the trap overflow. The extraction is complete when the level of water in the trap is constant and solvent dripping from the thimble is clear. Terminate the extraction and allow the apparatus to cool.

Calibration of Densimeter

6. Prepare a series of standard solutions of middlings and tailings bitumen in toluene covering the range 0.3 - 12 g/250 mL. (a)
7. Filter the standards through a 0.45 μm filter and determine the density of the solutions to six places.
8. Prepare a calibration curve by plotting the density of the standards versus the bitumen concentration in grams of bitumen per 250 mL. Calculate the slope and intercept of the plot using a linear least square regression. Coefficients of determination better than 0.999 are expected. The calibration does not have to be repeated daily, but several points on the calibration curve should be checked periodically to confirm the calibration.

Bitumen Determination

9. Disassemble the extraction apparatus and pour the bitumen/toluene extract into a 1000 mL volumetric flask and dilute to volume with toluene. Filter several millilitres of the solution through a 0.45 μm filter and determine its density to six decimal places. Ensure that the measured density falls within the range of the calibration.

Solids Determination

10. Remove the thimble from the extraction apparatus, place it in its beaker and dry for 12 hours at 120°C. Cool and reweigh.

Calculations: The bitumen, water and solids contents of the sample are given by:

$$\% \text{ Bitumen} = \frac{B}{W} \times 100$$

$$\% \text{ Solids} = \frac{S}{W} \times 100$$

$$\% \text{ Water} = 100 - (\text{wt \% Bitumen} + \text{wt \% Solids})$$

where: W = weight of sample, g

S = weight of solids recovered in thimble, g

$$B = \frac{\text{Sample Density} - \text{Calibration Intercept}}{\text{Calibration Slope}} \times 4$$

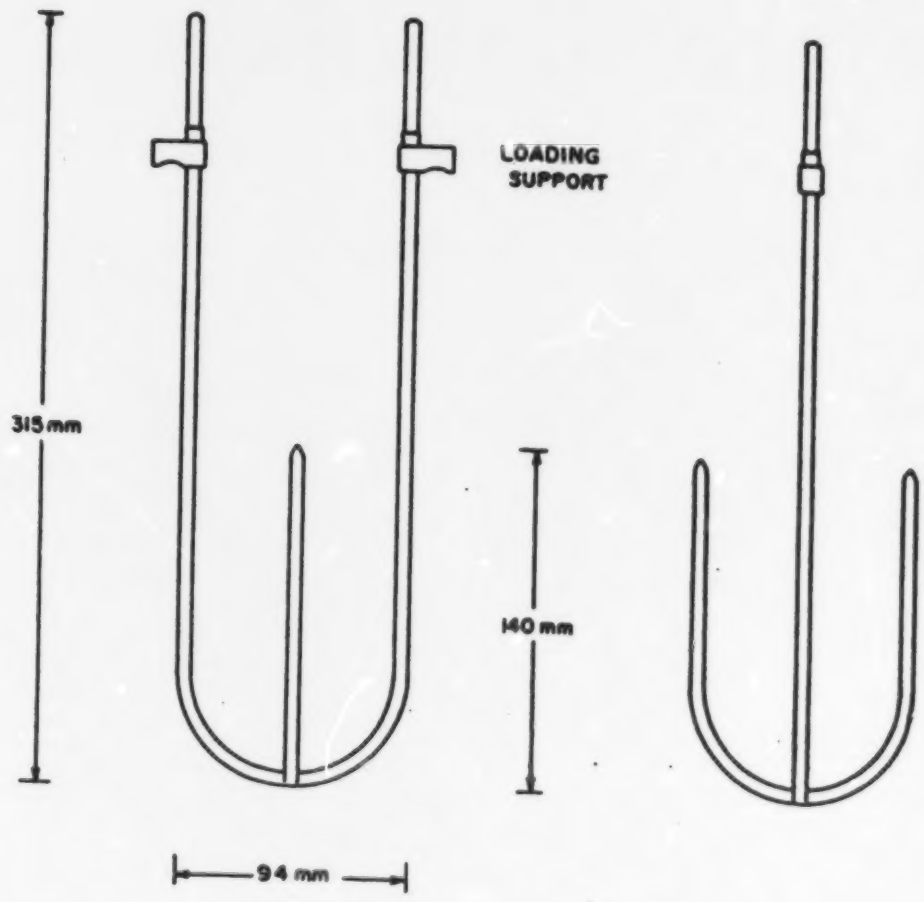
= weight of bitumen in sample, g

Precision: Data tabulated below indicates typical precision values associated with the bitumen, water and solids analysis of middlings and tailings samples. Estimates reflecting the repeatability of a middlings analysis were determined on 37 replicate subsamples prepared by Method 1.6 and analyzed using the small extractor assemblies. Precision values for primary and secondary tailings were evaluated from 10 replicate samples obtained in rapid succession from pilot plant process streams and analyzed using large extractor assemblies. All data includes errors due to sampling.

	Mean Value (wt%)	Standard Deviation (wt%)	Relative Standard Deviation
Middlings			
Bitumen	7.32	±0.15	2.05%
Water	75.91	±0.42	0.55%
Solids	16.77	±0.38	2.27%
Primary Tailings			
Bitumen	0.87	±0.06	6.90%
Water	35.01	±1.47	4.20%
Solids	64.12	±1.48	2.31%
Secondary Tailings			
Bitumen	0.44	±0.02	4.55%
Water	79.98	±1.71	2.14%
Solids	19.58	±1.71	8.73%

Comments:

a. The bitumen for the standard solutions is prepared by extracting a large number of middlings and tailings samples on a solids extraction apparatus, removing non-filtered solids by centrifuging, removing toluene by evaporation, and determining the residual toluene content by the procedure described in Method 2.7.



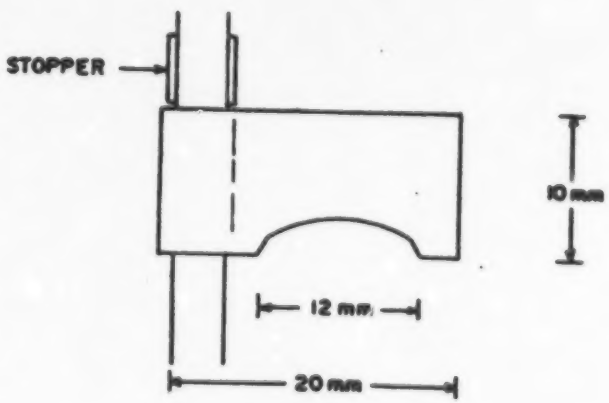


FIGURE 1: EXTRACTION THIMBLE BASKET

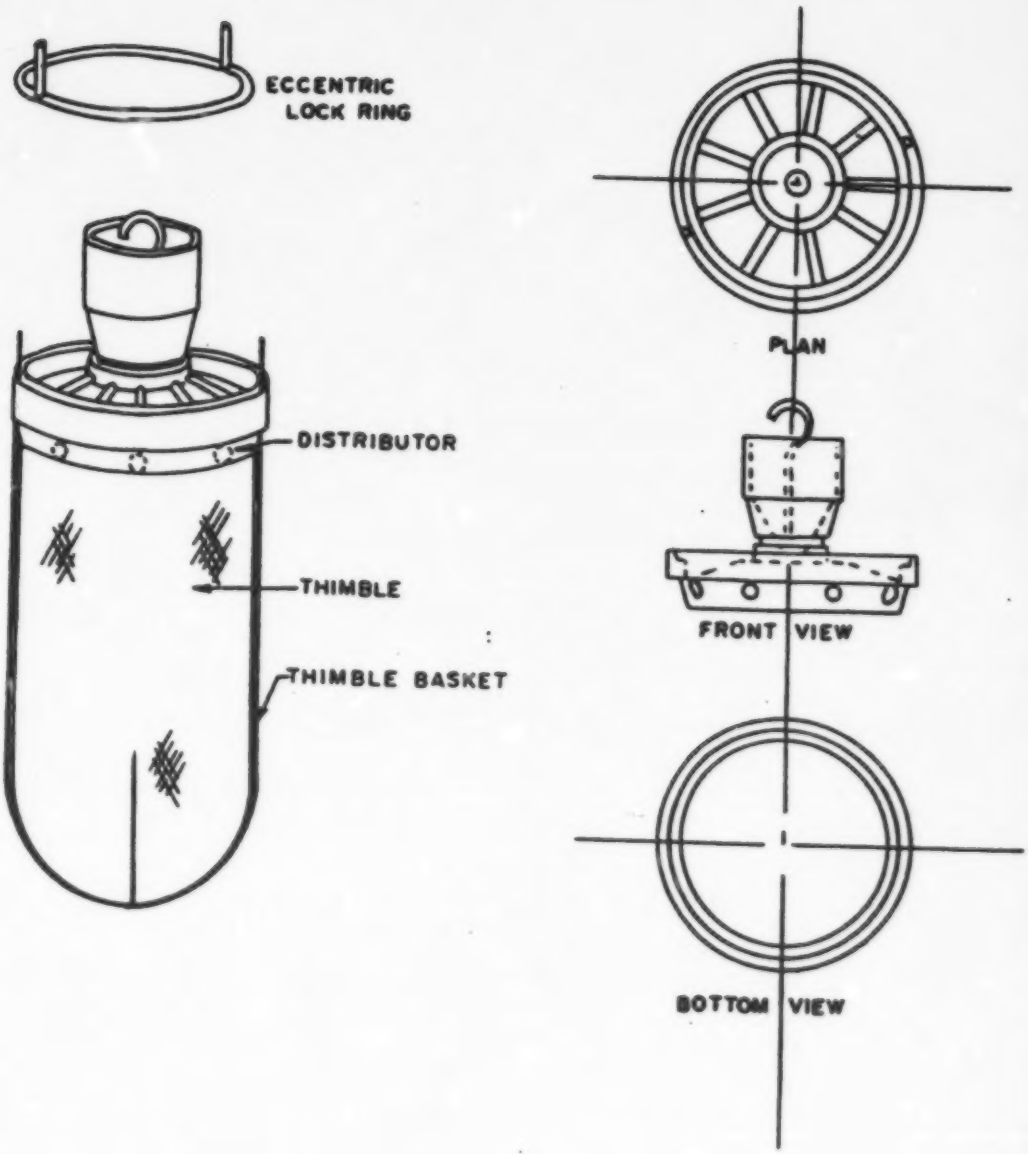


FIGURE 2: THIMBLE ASSEMBLY AND SOLVENT DISTRIBUTOR

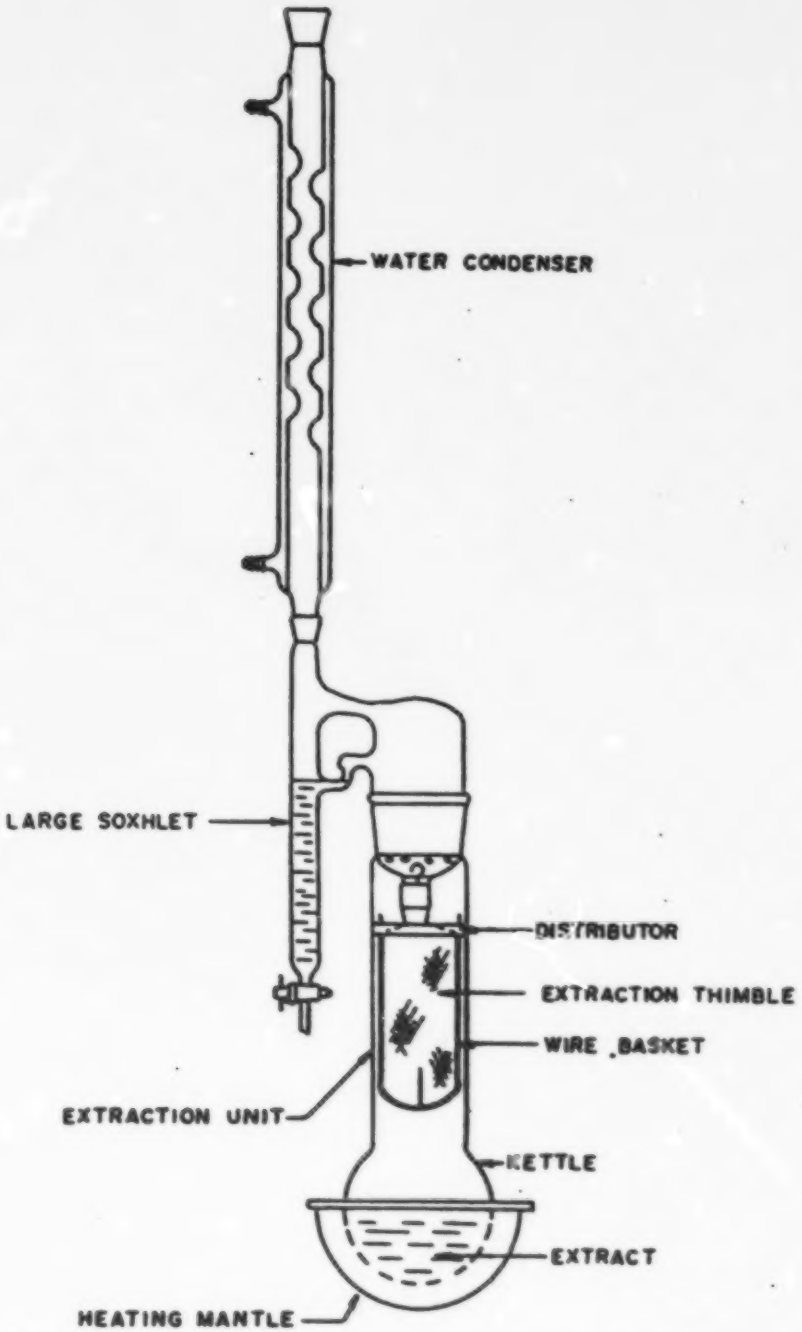


FIGURE 3: EXTRACTION APPARATUS

APPENDIX B

RESULTS OF PAH'S AND METAL ANALYSES PERFORMED BY CORE LABS

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CORE LABORATORIES

COMPANY Nova Husky Research Corporation Ltd.

FILE 52141-89-491
DATE 1989 04 20

Sample Identification

491-1	Prince George February 14
491-2	Prince George Compost December 14
491-3	Trap 1 April 3
491-4	Trap 2 April 1
491-5	Trap 3 April 1
491-6	Reactor 2 February 16
491-7	Reactor 3 February 16
491-8	Reactor 3 April 1
491-9	Reactor 2 April 1
491-10	Reactor 1 April
491-11	0.75 Desalter April 1
491-12	0.75 Deslater March 3

CORE LABORATORIES

COMPANY Nova Husky Research Corporation Ltd.

FILE 52141-89-491
DATE 1989 04 20

Date Received: 1989 04 05
Date Analyzed: 1989 04 15

PAH Analytical Results (ug/L)

Quantified Components	491-6	491-7	491-8	491-9	491-10
Naphthalene	0.6	1.3	-	-	5.8
2-Methylnaphthalene	0.8	1.3	-	2.3	190
Acenaphthylene	-	-	-	-	IF
Acenaphthene	-	-	-	-	69
Dibenzofuran	-	-	-	-	50
Fluorene	-	-	-	-	210
Phenanthrene	1.3	-	-	5.7	140
Anthracene	-	-	-	-	25
Carbazole	-	-	-	-	IF
Fluoranthene	-	-	-	-	IF
Pyrene	-	-	-	3.2	24
Benz[a]anthracene	-	-	-	-	11
Chrysene/Triphenylene	-	-	-	2.3	55
Benzo[b]fluoranthene	IF	-	-	IF	IF
Benzo[a]pyrene	IF	-	-	IF	IF
Ideno[1,2,3-cd]pyrene	-	-	-	-	IF
Dibenz[a,h]anthracene	-	-	-	-	IF
Benzo[ghi]perylene	-	-	-	-	IF
Semiquantified Components					
1-Methylnaphthalene	0.4	0.6	-	2.8	190
Dimethylnaphthalenes	5.8	1.9	-	43	1100
Methylphenanthrenes and Methylanthracenes	7.1	-	-	27	1000
2-Methylfluorene	-	-	-	-	230
1-Methylfluorene	-	-	-	-	280
Dibenzothiophene	-	-	-	-	330

Analyst

Phillip Oltman, Ph.D.

Susan Riley

Susan Riley, B.Sc.

Ltd.

PAGE 5 of 6
FILE 52141-89-491
DATE 1989 04 20

COMPANY Nova Husky Research Corporation Ltd.

Date Received: 1989 04 05
Date Analyzed: 1989 04 15

alysis (mg/L)

Trace Metals Analysi

491-6	491-7	Element	491-8	491-9	491-10	49
0.06	<0.03	Aluminum	<0.03	0.03	0.03	<0.
<0.05	<0.05	Arsenic	<0.05	<0.05	<0.05	0.
<0.001	<0.001	Barium	<0.001	<0.001	<0.001	0.
<0.001	<0.001	Beryllium	<0.001	<0.001	<0.001	<0.
0.14	<0.01	Boron	<0.01	<0.01	<0.01	<0.
<0.002	<0.002	Cadmium	<0.002	<0.002	<0.002	<0.
43	42	Calcium	11	7.6	4.2	9.
0.13	0.11	Chromium	0.053	0.042	0.026	0.
<0.003	<0.003	Cobalt	<0.003	<0.003	<0.003	<0.
<0.002	<0.002	Copper	0.012	0.025	0.017	0.
0.21	0.16	Iron	0.15	0.14	0.15	1.
<0.03	<0.03	Lead	<0.03	<0.03	<0.03	<0.
55	53	Magnesium	18	11	5.0	13
4.4	4.2	Manganese	1.3	0.7	0.38	0.
<0.005	<0.005	Molybdenum	<0.005	0.008	<0.005	0.
<0.01	<0.01	Nickel	<0.01	<0.01	<0.01	<0.
3700	3400	Phosphorus	1800	1400	890	2800
3500	3300	Potassium	1900	1400	910	2800
10	9.6	Silicon	8.2	6.5	2.2	22
0.035	0.036	Silver	0.028	0.028	0.017	<0.
750	590	Sodium	350	310	220	-
<0.05	<0.05	Thallium	0.06	<0.05	<0.05	<0
<0.02	<0.02	Tin	<0.02	<0.02	<0.02	0.
<0.002	<0.002	Titanium	<0.002	<0.002	<0.002	<0.
<0.005	<0.005	Vanadium	<0.005	<0.005	<0.005	<0.
0.09	0.07	Zinc	<0.01	<0.01	0.02	<0.

Analyst: J C Banks
John Banks, B.Sc.

APPENDIX C

BACTERIA PRESENT IN THE REACTORS OVER THE STUDY PERIOD

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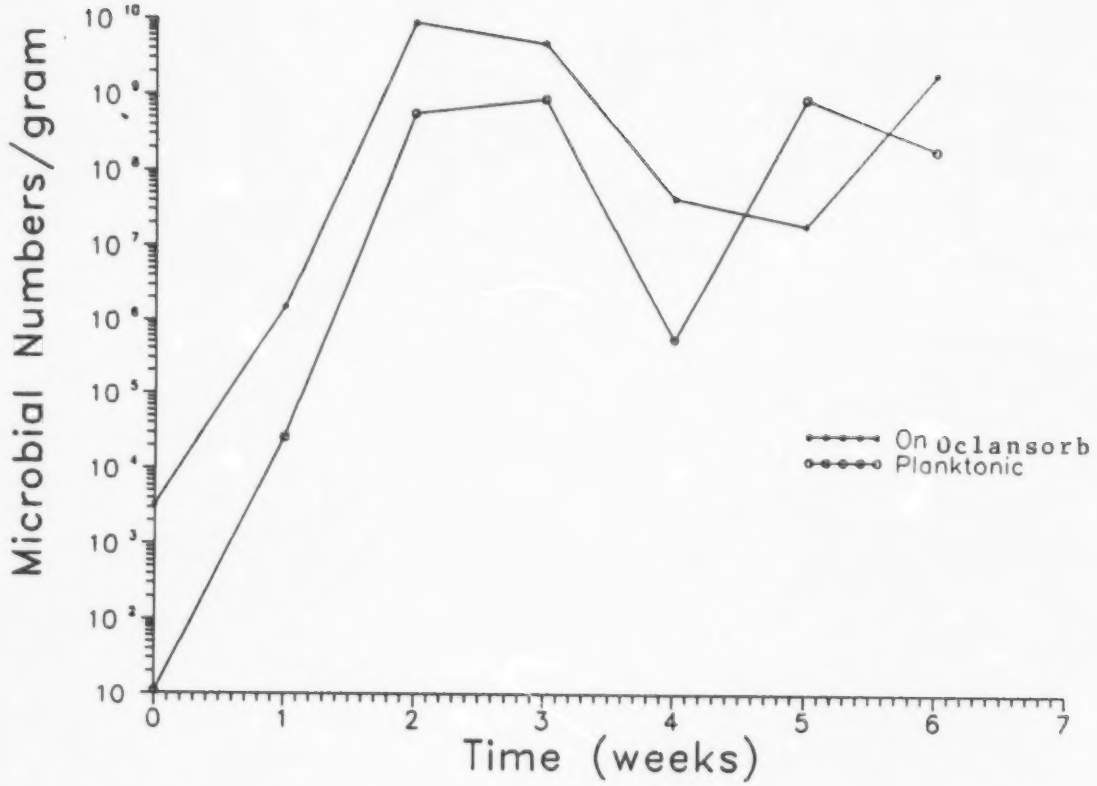
REACTOR 1



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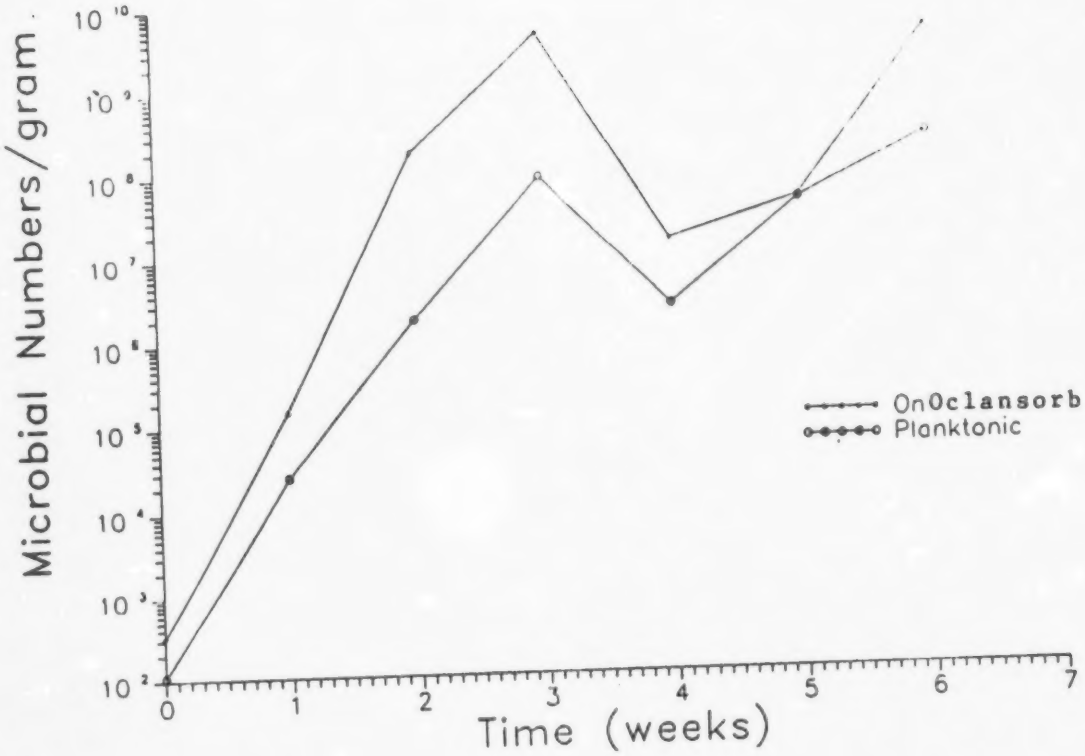
REACTOR 2



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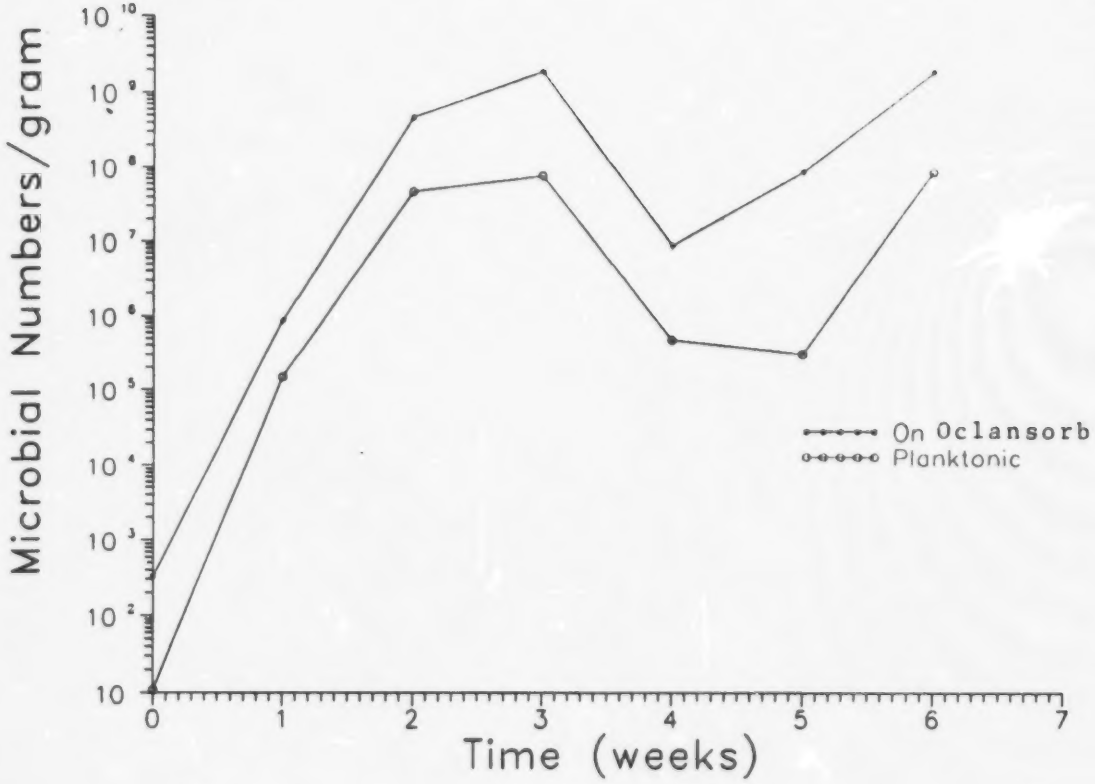
REACTOR 3



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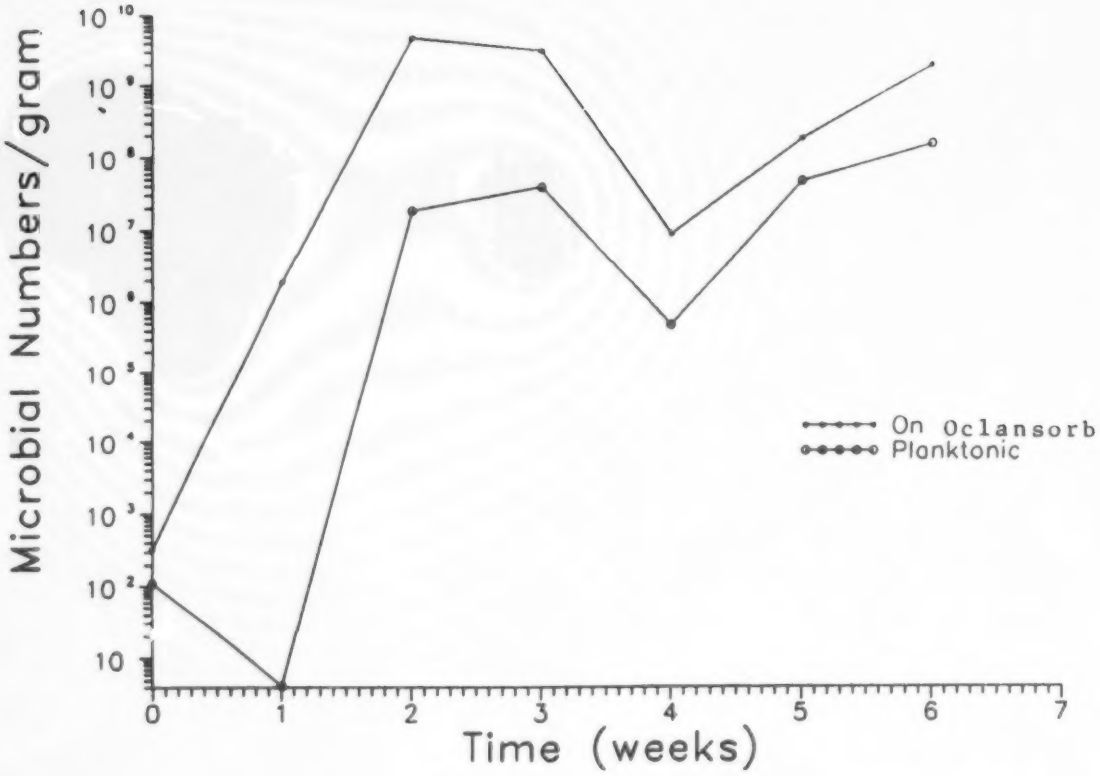
0.75 MOLES $KMnO_4$/KG



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APPENDIX D

UV SCANS OF NAPHTHALENE TREATED WITH PERMANGANATE IN HEXANE

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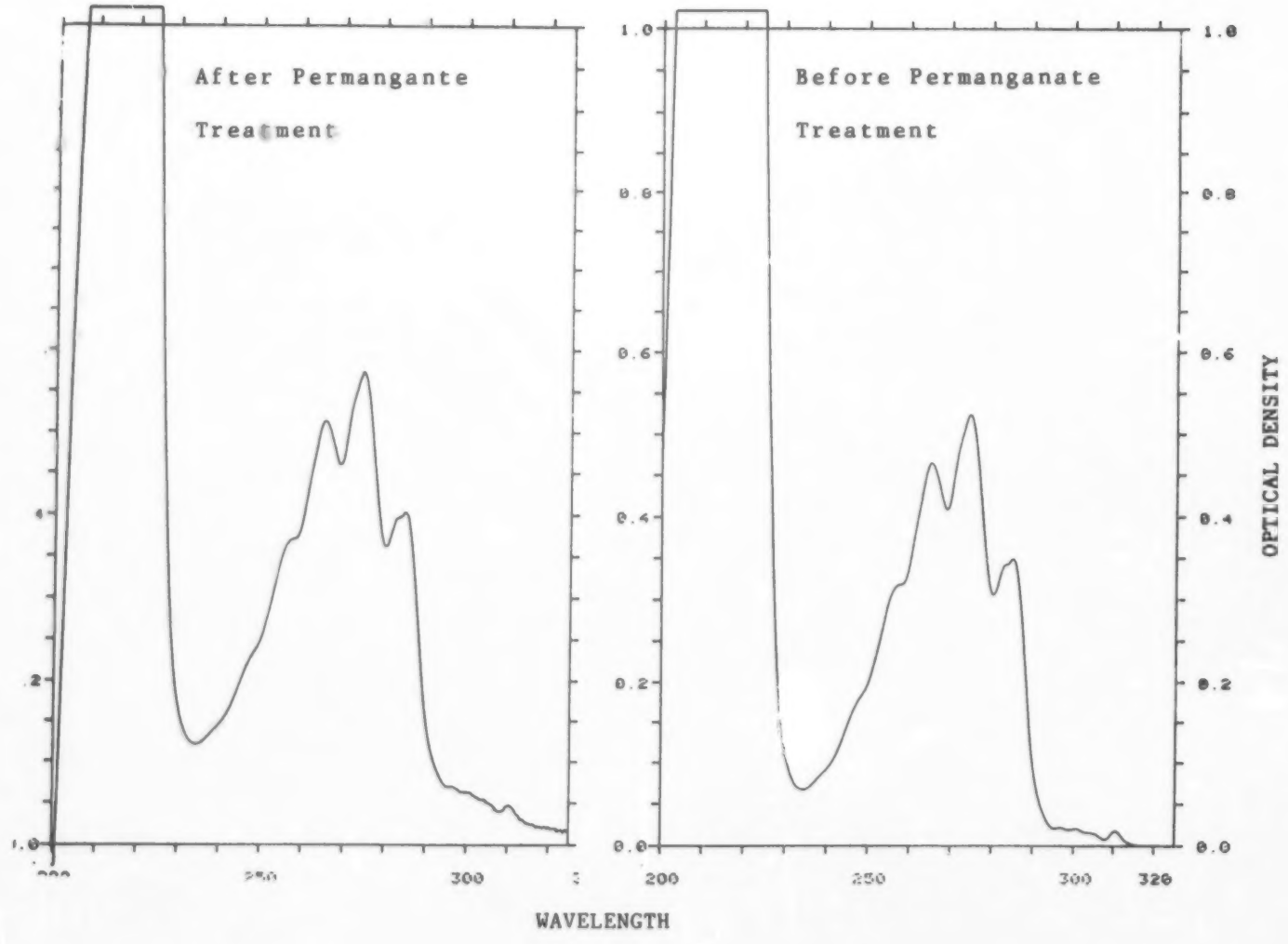

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